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CARBON COMBUSTIONS IN A PLATINUM CRUCIBLE.

BY P. W. SHIMER.

Received February 14, 1899.

THE determination of carbon by combustion in oxygen necessitates the use of a costly and bulky combustion furnace, a porcelain or platinum tube, and a supply of pure oxygen. The gas consumption is large and the heat generated is ridiculously out of proportion to the small amount of carbon to be burned. Even with this wasteful use of gas, the temperature attained, under the conditions of gas pressure existing in some laboratories, is not always high enough to ensure the complete combustion of graphite in pig iron.

In the apparatus devised by the writer, it is proposed to use a platinum crucible, with a water-cooled stopper, in place of the porcelain or platinum tube; an ordinary small blast-lamp and Bunsen burner in place of the combustion furnace; and air instead of oxygen.

The crucible is a platinum fusion crucible of the usual shape, about $1\frac{7}{16}$ inches in diameter and $1\frac{9}{16}$ inches high. In order to stiffen the top of the crucible, a ring made of ordinary sheet copper about $\frac{3}{16}$ inch wide, brazed at the ends, is fitted closely around the extreme top of the crucible. This ring is made of sheet metal so as to give the crucible the necessary support against stretching, without, at the same time, making it too rigid.

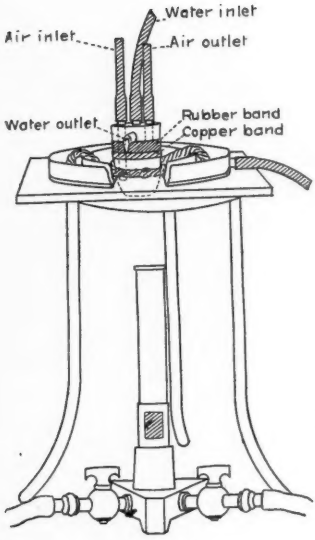


Fig. 1.

Fig. 2.

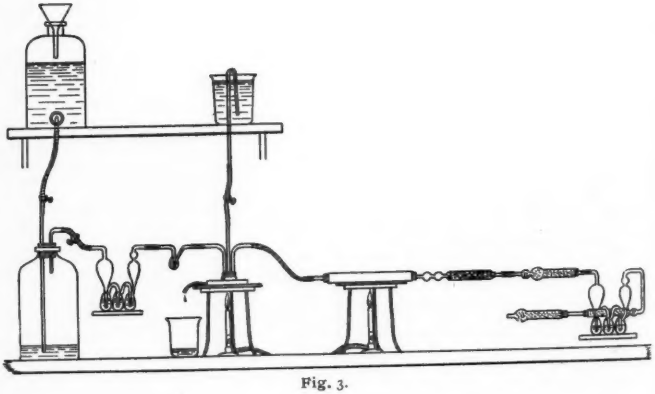


Fig. 3.

The essential part of the apparatus is the water-cooled stopper for closing the crucible. The construction of this stopper will be readily understood from the sketch. The stopper is made of sheet copper, the joints being brazed. It is, of course, essential that it should be as near perfectly circular as possible, with no indentations or imperfections in the brazing. The sides of the stopper should not flare more than the sides of the crucible at the top. Too much flare has a tendency to cause the stopper to be forced out of the crucible when under pressure.

The stopper is made somewhat smaller than the crucible opening, in order to allow space for a rubber band. This band is of pure black rubber such as can readily be obtained at most stationers. It is one-fourth to one-half inch wide and of such a length that it will stretch tightly around the lower part of the stopper. With a very little experience in putting the rubber-banded stopper into the crucible, it may be made perfectly tight with a greater degree of certainty than can the common rubber stoppers used in a porcelain combustion tube.

When the lower part of the crucible comes to a bright red heat in the course of a combustion, there is no risk whatever of burning or softening the rubber, for the band is cooled by the water passing through the stopper and by wet wick wrapped twice or more around the upper part of the crucible, the ends of the wick drawing their water from a circular copper trough kept full by the overflow from the stopper. In order to avoid any risk of softening the lower edge of the band by the heat radiating from the bottom of the crucible, the latter is always one-third to one-half full of ignited asbestos. I have used a single rubber band for as many as twenty combustions, and then discarded it only because it was becoming hard, making it more difficult to make the crucible tight.

In the train for the combustion of carbon in iron and steel, shown in the illustration, we have the following parts, beginning at the left:

1. Two aspirator bottles, the upper filled with distilled water and the tube leading to the lower bottle extending to the bottom of the latter.

2. Potassium hydroxide bulbs containing potassium hydroxide of 1.27 specific gravity.

3. A little guard bottle to retain any drops of potassium hydroxide that may be forced over from the Geissler bulbs.

4. The combustion crucible connected with its reservoir of *distilled* water for supplying the stopper; the circular trough to catch the overflow and serve as a source of water for the wet wick; the piece of stout asbestos board perforated to support the crucible at a point about half way through. Under the crucible we have the blast-lamp.

5. Next to the crucible is the cupric oxide tube, a short brass or porcelain tube, ten to twelve inches long, of small diameter. In some recent experiments, a small brass tube three-eighths inch in diameter and ten inches long, filled in its middle portion with cupric oxide, was tried in place of the porcelain tube and was found to be quite satisfactory. The brass tube is filed down at the ends and the rubber tubing is stretched over them. Although a porcelain tube is shown in the sketch, I am now using a brass tube altogether. The cupric oxide tube is supported across the top of a tripod, with a single good Bunsen burner below, to heat to a red heat one and one-half to two inches of the cupric oxide. A piece of stout asbestos board is laid across the top of the tripod to retain the heat.

6. Next to the cupric oxide tube is a glass tube filled with glass beads, wet with water and kept quite cold externally by wet wick, to retain chlorine and hydrochloric acid. The wick is wrapped about the tube, the free ends hanging in a beaker of distilled water, not shown in sketch.

7. A large calcium chloride tube.

8. The potassium hydroxide bulbs with calcium chloride tube attached.

9. A guard tube of calcium chloride.

In the preliminary experiments some trouble was experienced in getting satisfactory constant weights on the potassium hydroxide bulbs. There was a constant increase in weight. After excluding all the sources of error that at first suggested themselves, there still remained an increase in weight of from 0.0007 to 0.0018 gram. In these early experiments air was *drawn* through the apparatus. It now occurred to me that possibly the permeability of platinum at a red heat was the cause of the trouble. Air was then forced through the apparatus, with the

result that the constant weights very rarely differed more than 0.0005 gram.

It might be supposed, if platinum is permeable at a red heat, that there would be loss of carbon when pressure is used. When, however, we compare the comparatively small amount of carbon drawn into the crucible when immersed in the flame, with the large total amount of carbon burned in the flame, and then imagine a like proportion of the small weight of carbon in the crucible lost by permeation, we may conclude that the loss is inappreciable. At all events the carbon results obtained in this way agree closely with standard results obtained by combustion in a porcelain tube in oxygen. Besides, if permeability of platinum is a serious matter in carbon determinations, it is strange that the users of platinum combustion tubes have not discovered it.

In the course of these constant weight experiments, it may be interesting to note in passing, the now well-known difficulty of getting closely agreeing constant weights in stormy weather was again noticed. Another source of error in getting constant weights was noted when, on one occasion, the hydrant water used in the aspirator bottles had become somewhat stagnant. There were enough gaseous products of decomposition, or of animalcular life processes, to cause increase in weight of the potassium hydroxide bulbs, which ceased as soon as distilled water was used in the aspirator bottles. These gases passed through the first potassium hydroxide bulbs and were burned to carbon dioxide in the crucible and cupric oxide tube and were then, of course, absorbed by the weighed potassium hydroxide bulbs.

The method of solution of steel for carbon determination is the standard one by use of acidified solution of double chloride of copper and potassium. The carbon is filtered upon asbestos in the following manner: A glass rod about one inch longer than the stem of the funnel (an ordinary funnel, two and one-half inches in diameter) and small enough in diameter to pass easily through the stem, is flattened out at one end and notched at two or three places by pressing the red hot glass against the sharp corner of a file. The sketch shows the flattened and notched end of the rod; also the rod in position in the stem of the funnel.

In preparing the filter, very short fibered ignited asbestos is used, with fibers not longer than one-sixteenth inch. This is well stirred up with distilled water so as to have it well in suspension in a rather large bulk of water. A small piece of dry asbestos about the size of a pea is placed in the bottom of the funnel upon the end of the glass rod. This is to prevent the finely divided and suspended asbestos from packing into the passage, thus impeding filtration. The suction is now turned on and a little of the suspended asbestos is poured on. When this has been deposited as a fine horizontal felt, pour on more asbestos. If the asbestos fibers are short enough, a perfectly tight filter may be made with not more than one-fourth inch of asbestos. A small bulk of filter greatly facilitates subsequent transference and combustion. When dry, the carbon may usually be picked off in a thin shell by means of a pair of forceps. It is easily transferred to the empty crucible, *with the carbon side down*. It is well to have a circular piece of thin platinum foil in the bottom of the crucible. The small amount of carbon remaining in the funnel is removed by use of a little ignited asbestos. It is necessary to be careful to keep all the carbon within about one-fourth inch from the bottom of the crucible, which is not at all difficult to do. If a part of the carbon were to be one-half to three-fourths inch from the bottom, it might escape complete combustion. Graphitic carbon from pig iron is easily burned in air at the white heat attainable by the blast-lamp. After the carbon is all transferred, a little ignited asbestos is filled in on top of it.

Another way is to add a little finely divided, ignited asbestos to the solution, and to filter the carbon on a Gooch crucible. The Gooch, without its cap, is then placed on the bottom of the combustion crucible. This method has the advantage of rapid filtration, quick transference, and avoidance of contact of the carbon and traces of copper oxide with the bottom of the combustion crucible. A Gooch crucible may be made out of an old ignition crucible.

There is no reason why oxygen should not be used successfully, but, when air does the work effectually, it seems unnecessary to use oxygen. An advantage of air is that the bulbs are weighed filled with air before and after the combustion, and

there is no need to replace oxygen with air as in the oxygen method.

When getting constant weight, proceed as follows: Fill the crucible one-third full of ignited asbestos and close it, first wetting the rubber band. Saturate the wick with alcohol; it is difficult to wet it with water. Wrap a long piece of the wick twice or more *closely* around the crucible as it rests in its place in the asbestos board, and allow the ends of the wick to lie in the copper trough as shown in the sketch. When a brass cupric oxide tube is used, a little wet wick wrapped several times about each end inside of the rubber connections and hanging in beakers of water, will avoid all risk of burning. The moisture tube is disconnected and filled with cold distilled water and the excess is allowed to drain out by holding the tube in a vertical position. It is then connected as shown in the sketch. Open the clamp and allow water to run out of the stopper. Now put the Bunsen flame under the crucible and the middle of the cupric oxide tube, covering the latter with a piece of asbestos board. Open the Hofmann clamp between the upper and lower aspirator bottles and leave it fully open. Open the Hofmann clamp between the lower aspirator bottle and the potassium hydroxide bulb and regulate the passage of air by this clamp alone. Let air bubble through the apparatus, rather more rapidly than in oxygen combustion, for twenty minutes. Detach and weigh with the usual precautions. A second weight nearly always agrees well with the first. My constant weights with this apparatus have deen steadily better than I have ever been able to get with the combustion furnace and oxygen, which may be attributed both to the use of air all through and to the absence of the disturbing influence of the hot furnace near the bulbs to be weighed, and the moisture-laden air resulting from the burning of large volumes of gas. When the constant weight is obtained, the carbon is transferred to the crucible as described and the combustion is begun, after, of course, testing the apparatus for tightness. Before putting the stopper into the crucible it is best to wet the rubber band with the wet finger. This prevents friction and ensures a tight crucible. In putting in the stopper do not brace the thumb against the overflow tube, for there is great risk of bending the stopper at the base of the over-

flow. Be sure that water is running from the stopper and that the cupric oxide tube is red hot for from one and one-half to two inches, then turn on the air at the speed of about three bubbles per second and bring a small blast-lamp flame immediately under the crucible so as to heat the bottom to a bright red heat, extending at least one-fourth inch from the bottom. A large flame is to be avoided. The bottom of the crucible should be flat or, better, slightly convex—*never concave*. Combustion begins immediately, and in one or two minutes carbon dioxide begins to be absorbed by the potassium hydroxide bulbs. Combustion is complete in twenty-five minutes or less. In removing the asbestos from the crucible there is often, when copper solution has been used for dissolving the sample, a black residue remaining where the carbon was, which may mislead the inexperienced, but it is oxide of copper, as is easily proved by its solubility in strong hydrochloric acid.

When the carbon, after filtration, is well washed both with hydrochloric acid and hot water, there is very little chlorine or hydrochloric acid to fear, and the moisture tube effectually stops it. After every five or six combustions, it is only necessary to rinse out the tube with distilled water and connect it again. This moisture tube has been in use in my laboratory for several years, and it has proved itself a simple and efficient means of retaining chlorine and hydrochloric acid. The tube was made for me by Greiner; it is six inches long and three-fourths inch in diameter. The two bulbs are empty; the tube itself is filled with glass beads of about one-eighth inch in diameter. The tube retains about two and a half cc. water when drained. In some experiments an acid solution of silver sulphate was used in place of water, but, under the conditions, it was not more effective than water.

It may be interesting to note here that in some experiments made to determine how near the carbon could be determined by use of the crucible without the cupric oxide tube, it was found, as was of course to be expected, that only about ninety per cent. of the carbon was oxidized to carbon dioxide and determined. Another experiment in which asbestos coated with cupric oxide was placed on top of the carbon in the crucible, without the cupric

oxide tube, gave much better results, but still slightly below the correct figures.

The following are a few carbon determinations:

	By combustion in a porcelain tube in oxygen.	By combustion in air in crucible.		
Steel A	1.035	1.034	1.035	1.039
" B	1.040		1.046	
" C	1.032		1.029	
" D	0.466		0.466	

DUPLICATE RESULTS BY COMBUSTION IN AIR IN CRUCIBLE.

Graphite in pig iron	3.327	3.334
Soft steel E	0.026	0.026
" " F	0.023	0.023
Steel G	0.188	0.187
" H	0.580	0.582

By the kindness of Mr. C. A. Buck, chemist of the Bethlehem Iron Co., I am able to give the following series of carbon results obtained by him while testing the reliability of the combustion apparatus preparatory to using it regularly in the laboratory of the Bethlehem Iron Co. For steels Mr. Buck uses fifteen minutes' combustion and five minutes' aspiration. For pig irons he uses twenty-five minutes' combustion. The results are as follows, on standard samples:

	Combustions in platinum tube.	Combustions in crucible.	Average.
Steel No. 1	1.060	1.059	
		1.058	
		1.064	
		1.066	
		1.060	
		1.063	
		1.063	
			1.062
Steel No. 2	0.490	0.491	
		0.496	
		0.488	
		0.493	
		0.490	
		0.487	
		0.488	
			0.490

	Combustions in platinum tube.	Combustions in crucible.	Average.
Steel No. 3.....	0.183	0.178	
		0.184	
		0.189	
		0.179	
		0.180	
			0.182
Steel No. 4.....	1.020	1.020	
		1.020	
		1.025	
			1.022
Steel No. 5.....	0.700	0.696	
		0.699	
			0.698
Pig iron No. 1—Total carbon..	3.670		3.690
Pig iron No. 2 " "	3.638	3.600	
		3.620	
		3.646	
		3.620	
			3.622

The crucible may also be used in the determination of carbonic acid and combined water in ores, limestone, etc. For these determinations the apparatus is arranged in the following order: The air passes first through the potassium hydroxide bulbs, then through a calcium chloride tube, then through the crucible containing the dried sample, preferably contained in a small basket of platinum foil fitting closely into the bottom of the crucible. Next to the crucible is the weighed calcium chloride tube and following this the potassium hydroxide bulbs and guard tube of calcium chloride. In determining water, it is necessary to heat the water in the beaker supplying the stopper in order to prevent condensation of moisture on it. Constant weights obtained on the calcium chloride tube with the stopper supplied with hot water agree within 0.0001 to 0.0003 gram, while, with cold water in the stopper, the increase of weight was sometimes as high as 0.0040 gram. The water condensed on the stopper would, to an appreciable extent, be drawn down under the rubber band.

In determining carbonic acid in limestone, one gram of the finely ground sample is placed in the bottom of the crucible and on top of this is placed a layer of ignited asbestos. The ignition

is maintained for a half hour. In determining water alone, there is, after the crucible, only the weighed calcium chloride tube and the guard tube of calcium chloride. The following are some results on carbon dioxide and water.

	Carbon dioxide. I.	II.	Water.
In zinc ore A	7.80–7.94		0.60
" " " B	1.35		1.12
" " " C	7.68		1.22
" " " D	1.23–1.21		0.76
" " " E	2.76		0.71
" " " F	2.58		0.55

Mr. J. W. Louder obtained the following results in determining carbon dioxide and water :

	Carbon dioxide. I.	II.	III.
In limestone A	45.80	45.65	45.62
" " B	44.29	44.38	....
	Water. I.	II.	III.
In selenite	20.13	20.12	20.23

The crucible has also been used in determining iron in iron ore by reduction in hydrogen at a red heat, solution of the reduced iron in sulphuric acid and titration with permanganate solution. In the arrangement of the apparatus for this purpose, the hydrogen is passed from the evolution flask through a wash-bottle containing strong sulphuric acid. Then through the crucible containing one-half gram of the dry ore weighed out into a small basket of platinum foil fitting the bottom of the crucible.

The ore should be roasted in air in the open crucible for about five minutes to destroy any carbonaceous matter present. It is allowed to cool and then the stopper is inserted and hydrogen is passed through the apparatus. When all air has been expelled, the crucible is heated to a red heat for one-half hour, allowed to cool perfectly in the hydrogen current, then dissolved in sulphuric acid and titrated. This method, while accurate for ores containing no iron in the insoluble residue, has no advantage over some of the more rapid methods. An Alabama hematite containing 48.36 per cent. total iron (48.24 per cent. soluble in hydrochloric acid, and 0.12 per cent. insoluble in hydrochloric

acid) gave, by reduction in hydrogen, 48.26 per cent. iron, showing complete reduction of all the iron but the small amount present in a combination insoluble in hydrochloric acid. This method is not recommended for general use, but is given merely as an illustration of the widely various uses to which the crucible may be put.

It is, however, not adapted for those organic combustions in which condensible decomposition products are formed. These condense in the cooler upper part of the crucible where they are beyond reach of the temperature necessary to burn them. Probably by mixing such organic compounds with suitable oxidizing material, such combustions might be successfully made, but this is a field that has not yet been investigated

My last combustion apparatus was made for me by the Baker and Adamson Chemical Co., of Easton, Pa., who also furnished me with a reliable quality of pure rubber bands.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, NO. 34.]

THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC ROTATION OF SUCROSE AND METHOD OF CORRECTING READINGS OF COMPENSATING POLARISCOPES THEREFOR.[1]

BY HARVEY W. WILEY.

Received March 9, 1899.

THE influence of temperature on the specific rotation of sucrose has been mentioned by several authors. A partial résumé of the literature on the subject is given by von Lippmann.[2] A more detailed discussion of the subject is given by Sachs.[3] A rather full abstract of previous papers on the subject is given by Sachs, who strangely, however, fails to mention the paper of Andrews on this subject. The early writers with the exception of Dubrunfaut[4] seem to be unanimously of the opinion that the temperature exerts no notable influence on specific rotation. This is the doctrine announced by Tuchschmidt[5] and

[1] Read before the American Chemical Society and Section C, of the American Association for the Advancement of Science, at Boston Meeting, August, 1898, and before the Third International Congress of Applied Chemistry, Vienna, August, 1898.

[2] *Chemie der Zuckerarten*, Edition *1895*, page 672.

[3] *Ztschr. Rübenzuckerind.*, **46**, 264.

[4] *J. prakt. Chem.*, **28**, 10.

[5] *Ztschr. Rübenzuckerind.*, (*1870*), 649.

Mitscherlich.[1] Sachs also cites the experiments of Wachtel,[2] who explained the difference in polarization under the influence of temperature by ascribing it to the expansion of the quartz plates of the compensating polariscopes used. This explanation is evidently insufficient, and, as will appear further on, erroneous.

Petrucci and Sachs,[3] in 1889, also observed differences in polarization, due to temperature, and these observations were corroborated by Wartze.[4]

The experiments of Sachs were conducted by making the sugar solution at a given temperature and then polarizing it at other temperatures, and also by making up the sugar solution at the same temperature at which it was polarized. As a result of his investigations, he concludes that a solution of practically pure sugar, made up at 17.5°, and polarized at 17.5°, will show a decreased polarization of 0.20° Ventzke, when made up at 25° and polarized at 25°.

The causes of variation in polarizations in the trade were considered in a convention of technical chemists held in Berlin in 1895.[5]

In the United States the first corrections which were employed for variations in polarizations due to temperature were those ascertained by the Office of Weights and Measures of the United States Coast and Geodetic Survey in 1890, and adopted by the commission appointed by the Secretary of the Treasury to prepare regulations for use in the Bureau of Internal Revenue of the Treasury Department. The total correction due to variations in temperature for each degree C., as prescribed by the regulations, was 0.0293° Ventzke for a sugar polarizing 100° Ventzke. This correction was uniformly employed in the Bureau of Internal Revenue, in polarizations for determining the amount of bounty to be paid on domestic sugar in the United States, during the whole time in which the act granting such bounty was in force. It appears, therefore, that the first practical application of a correction for variations in temperature in sugar polarizations was applied in the United States.

[1] *Berl. Acad. Ber.*, (*1841*), 150.
[2] *Organ des Central-Verein*, Wien *1878*, 42.
[3] *Bull. Assoc. Belge Chim.*, 15 Febr., *1889*, 112.
[4] *Deutsche Zuckerind.*, 20 April, *1889*.
[5] *Ztschr. des Vereins für Rübenzuckerind.*, (*1895*), 1, 73.

A painstaking study of the influence of temperature on the polarization of cane-sugar was made by Andrews.[1] As a result of the investigations he deduced the following formula to express the influence of temperature on specific rotation:

$$[a]_D^t = [a]_D^{20} - 0.0114\ (t-20).^2$$

If 66.50 be taken as the mean value for $[a]_D^{20}$ the coefficient of change per degree C. is 0.000171,[3] which is somewhat smaller than that obtained by Dubrunfaut; namely, 0.000232.

The formula for calculation used by Andrews was

$$[a]_D^t = \frac{100\,a}{l \times p \times d'}$$

in which a = angle observed, in degrees;

l = length of tube, in decimeters;

p = percentage of sugar, by weight *in vacuo*.

d = specific gravity of the solution at temperature of observation, water at 4° C. being unity.

Dividing the total difference in rotation for different temperatures by the number of degrees of difference in the two sets of experiments conducted by Andrews, we have the following as the variation in the rotation for each degree C. in the two sets of experiments:

Difference per degree in the first set	0.0106
" " " " second set	0.0122
Mean of the two	0.0114

Andrews in his second paper[4] gives a table showing the factors for computing total variations in polarizations of solutions read at temperatures extending from 10° to 40°, both for direct and quartz compensation polariscopes. The mean factor for instruments without quartz compensation for each degree from 17.5° to 40° is 0.00018, and for quartz compensation instruments is 0.00030. These factors multiplied by 100 show the corrections for each degree of temperature for a pure sugar solution; *viz.*, 0.018 due to change in specific rotating power alone and 0.030 for total correction for quartz compensation instruments. These

[1] *Technology Quarterly*, Mass. Inst. of Technology, **2**, May, *1889*, 367.

[2] In Andrews' article the coefficient 0.0114 is given as 0.000114, but the context shows that this displacement of the decimal point is evidently a typographical error.

[3] This coefficient is obtained by dividing 0.0114 by 66.5.

[4] *Technological Quarterly*, May, 1889, **2**, 373.

figures are almost identical with those obtained in these investigations and given further on.

Schönrock[1] shows that temperature has a marked influence on the rotatory power of sucrose, which he expresses mathematically by the equation $\frac{d(a)}{dt} = -0.0144$, which may be expressed as follows: $[\alpha]_D^t = [\alpha]_D^{20} - 0.0144\ (t-20)$. By a solution of this equation he shows that the influence of temperature on rotation is one-fourth as great as that due to the change of volume of the liquid.

Landolt[2] elaborates the formula and shows that the change in polarization on the quartz wedge compensation polariscope, of a pure sugar solution, is equal to 0.065° V. for each degree of temperature. Of this 0.029° V. is due to the change of volume, leaving 0.036° V. due to the influence of temperature on polarization alone. These observations by Schönrock and Landolt were not seen by me until the work, on which this paper is based, was finished.

The recent changes in tariffs in the United States have resulted in a return to the polariscopic methods of ascertaining the percentage of sugar in imported sugars, with a view to levying duty in proportion thereto. I was designated by the Secretaries of the Treasury and Agriculture as chairman of a commission charged with preparing regulations for the control of the polarimetric work in the various ports of entry where sugars were received. It seemed advisable to make a new experimental study of the influence of temperature on the rotatory powers of sugars, especially in relation to the use of compensating polariscopes; *i. e.*, those instruments using a quartz wedge or wedges to restore the displacement of the plane of polarization produced by a sugar solution.

The instrument employed in these researches was a large triple shadow polariscope, double wedge compensation, made with the greatest care for the Department of Agriculture of the United States by Schmidt and Haensch, of Berlin.

The instrument was accompanied by three right-handed urnormal quartz plates, standardized by the Imperial Technical

[1] *Ztschr. für Instrumentenkunde*, 17, June, *1897*, 180.

[2] Das specifische Drehungsvermögen, Edition of 1898, pp. 344 *et seq.*

Institute at Charlottenburg. These plates were independently standardized by myself and my assistant, Dr. G. L. Spencer, in a large Landolt-Lippich monochromatic polariscope made by the firm above mentioned. The values in all cases were either determined at 17.5°, the standard temperature, or calculated thereto by accepted formulas. The values obtained by the three sets of independent observers are given in the following table:

Plate number.	Thickness determined by the Imperial Technical Institute. mm.	Rotation at 17.5°, determined by the Imperial Technical Institute. Angular degrees.	Rotation at 17.5°, determined by H. W. Wiley. Angular degrees.	Rotation at 17.5° determined by G. L. Spencer. Angular degrees.	Value on the Ventzke scale, determined by Schmidt and Haensch. °V.
1	1.4927	32.420	32.408	32.418	93.59
2	1.6020	34.777	34.748	34.739	100.36
3	1.2042	26.150	26.105	26.119	75.45

From the data supplied by the Imperial Technical Institute of Charlottenburg, and from the markings of the Ventzke scale by Schmidt and Haensch, the following conclusions are drawn:

(1) The rotation of a quartz plate one mm. in thickness at a temperature of 17.5° C. is equal to 21.7148°.

(2) The angular rotation of a quartz plate one mm. thick corresponds to 62.641 divisions on the Ventzke scale.

(3) One degree circular rotation corresponds to 2.8847 Ventzke scale.

(4) One degree of the Ventzke scale corresponds to 0.3465° angular rotation.

The mean determinations of the three independent observers for the three plates are as follows:

	Angular degrees.
Plate No. 1	32.415°
Plate No. 2	34.755°
Plate No. 3	26.125°

Determining the sugar factors[1] by the marked values of the plates, we get the following relations for the two sets of determinations, the data obtained by Wiley and Spencer being combined and compared with the data obtained from the Imperial Technical Institute of Charlottenburg.

[1] These factors are obtained by dividing each of the mean angular readings of the two series of observations by the marked value of the plate with which the observation was made.

Plate number.	Im. Tech. Institute determination. Angular degrees.	Sugar factor. 1° V= angular degrees.	Mean of Wiley and Spencer. Angular degrees.	Sugar factor. 1° V= angular degrees.	Marked °V.
1	32.420	0.34640°	32.413	0.34633°	93.59
2	34.777	0.34652°	34.744	0.34619°	100.36
3	26.150	0.34659°	26.112	0.34608°	75.45
	Mean	0.34650°	Mean	0.34620°	

We have then as the mean of the three factors obtained by the German authorities for converting angular rotation into degrees Ventzke 0.3465. For the same plates we have for the mean determinations secured by Wiley and Spencer the factor 0.3462. The difference between the two sets of determinations is insignificant, being only 0.0003. If now we use these factors for computing the sugar values of the quartz plates we have the following results from the German standard and from the mean standard as determined by Wiley and Spencer.

Plate number.	German rotation. Angular degrees.	Wiley and Spencer rotation. Angular degrees.	Calculated value of plate (German). °V.	Calculated value of plate (Wiley and Spencer). °V.	Marked value of plate. °V.
1	32.420	32.413	93.564	93.625	93.59
2	34.777	34.744	100.367	100.358	100.36
3	26.150	26.112	75.469	75.425	75.45

It is noticed that the variation of the results calculated from the mean factor from the marked values is very slight.

Being assured thus of the practical accuracy of the instrument employed and the control plates by which it was regulated, it was possible to begin the investigations looking to the determination of the influence of temperature on the specific rotatory power. Advantage was taken of the natural changes in the temperature during the period of investigation, to secure working periods of constant temperatures varying from each other by about 5° from 10° to 20°. Lower temperatures were secured, on the one hand, by conducting the experiments in a cold storage room, and on the other, higher temperatures were secured by means of artificial heat, keeping the atmosphere of the room thoroughly stirred by means of electric fans. In all cases the polariscope was exposed to the temperature of observation long enough to permit the various parts thereof to acquire the ambient temperature; *viz.*, from two to five hours.

For the purpose of having an absolutely unvarying quality of sugar solution, the whole of the material to be used was dissolved at one time into a thick sirup having almost exactly fifty per cent. of pure sugar and fifty per cent. of water. This sirup was preserved by having added to the water before solution an appropriate quantity of mercuric chloride. Double the normal quantity by weight of this solution was used in each determination. One flask, graduated with the greatest accuracy to a true Mohr flask at 17.5°, was used for all the determinations. With these sugars the following recorded observations were made. In each case, unless otherwise noted, five solutions were used and each solution was read four times, or more if there were errant readings, and the mean of the four concordant readings taken as representing the true reading.

In order to secure a better check on the readings, each set of readings was made in triplicate, one set with the white light telescope, one with the yellow light telescope, and one by inserting in the instrument a left-handed quartz plate of known value. The value of the control plate was determined by each of these methods and the necessary corrections made to bring them all up to the same standard of comparison. By adopting this method of triple readings any possible error of observation was eliminated. These triple readings were made in all cases, except the readings at 4° in the cold storage room, where, on account of the low temperature, it was deemed advisable to shorten the work by leaving out one of the sets of readings; *viz.*, the one checked against the left-handed quartz plate.

READINGS AT 4°.

On the afternoon of the 15th of April, 1898, readings were made at 4° in the cold storage room of the Washington Central Market, one of the rooms of which was kindly placed at our disposal by the superintendent.

Five solutions were read with the yellow and white lights. The term "yellow light" hereinafter employed refers to the readings with a telescope carrying a crystal of potassum bichromate or yellow glass plate, or with a tube containing a solution of potassium bichromate. On account of the absence of gas, in

the cold storage rooms, a kerosene lamp was used as the source of light. In all cases the temperature of the instrument and solutions was determined by a delicate thermometer, standardized by the Office of Weights and Measures of the Coast and Geodetic Survey. The readings of the right-handed quartz plate were as follows:

	°V.
With white light	100.20
With yellow light	100.24

The variations in the readings of the standard quartz plates, which will be noticed in the data here and following, aside from the nature of the light, are due to differences in setting the double quartz wedge compensation and not to changes in rotatory power. The readings of the sugar solutions with the yellow and white light were as follows:

Number.	Yellow light. °V.	White light. °V.
1	100.25	100.20
2	100.24	100.20
3	100.19	100.19
4	100.24	100.25
5	100.22	100.21
Means	100.23	100.21

Corrections: Add to the reading of the yellow light 0.12. Add to the reading of the white light 0.16.

These corrections here and following represent the differences between the observed reading of the urnormal quartz plate and its marked value; *viz.*, 100.36.

	°V.
Corrected means: Yellow light	100.35
White light	100.37
Mean of the two means	100.36

READINGS AT 10°.

On the night of April 14–15, between eleven and two o'clock, the external temperature sank to a little below 10°, and a series of readings was made at 10°. Preliminary readings were as follows:

	°V.
Right-handed plate, white light	100.33
Right-handed plate, yellow light	100.33
Right and left plates, white light	8.45
Difference in plates	91.88

	Readings of the sugar solutions with		
	quartz plate.[1] °V.	yellow light. °V.	white light. °V.
1	100.17	100.15	100.20
2	100.16	100.10	100.18
3	100.16	100.16	100.19
4	100.18	100.15	100.20
5	100.17	100.13	100.20
Means	100.17	100.14	100.19

Corrections: Add 0.03 to all mean readings. The corrected mean readings are:

	°V.
Solutions, with quartz plate	100.20
" " yellow light	100.17
" " white light	100.22
Mean	100.20

READINGS AT 15°.

A northwestern rainstorm on the morning of April 14 made it easily possible to secure a temperature of 15° in the observation room. A series of readings was therefore made at this temperature. The preliminary readings were as follows:

	°V.
Right-handed quartz plate, with white light	100.33
Right-handed quartz plate, with yellow light	100.29
Right-handed and left-handed quartz plates together, with white light	8.50

Difference between the two plates, $100.33 - 8.50 = 91.83$.

To facilitate observations and avoid changing the telescopes for white and yellow lights, a one-fourth per cent. solution of bichromate of potassium was prepared, with which a 100 mm. observation tube was filled and placed in the trough of the instrument, when it was desired to get a reading with yellow light. This gave a beautiful field, clearer than the yellow glass disk, and gave readings superior in every way to those made by means of the yellow light telescope.

	Readings of the solutions with		
	quartz plate. °V.	yellow light. °V.	white light. °V.
1	100.02	99.95	100.05
2	100.06	99.95	100.05
3	100.03	99.95	100.04
4	100.10	100.01	100.08
5	100.03	99.93	100.03
Means	100.05	99.96	100.05

[1] The readings entered here and following in column marked "quartz plate" are the observed readings of the solution with left-handed plate plus the difference between the reading of the right- and left-handed plates together. In this case the observed reading of solution No. 1, was 8.29. The reading of the solution is $8.29 + 91.88$, the difference between the two plates.

Corrections: Add 0.03 to the readings with the quartz plate and white light telescope, and 0.07 to the readings with the yellow light telescope.

	Corrected means. °V.
Solutions, with quartz plate	100.08
" " yellow light	100.03
" " white light	100.08
Mean of means	100.06

Variation from the mean reading at 20°, 0.18.

READINGS AT 20°.

On the morning of April 13, the temperature of the polariscope room being at 20°, four samples were polarized at the temperature mentioned. The reading of the right-handed plate by the plain telescope was 100.32; by the yellow eye-piece, 100.28. The reading of the two plates by the white light telescope was 8.46, showing the true value of the left-handed plate at the temperature mentioned to be 91.86.

The mean readings of the four samples were as follows:

	Readings of sugar solutions with		
	quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.89	99.71	99.86
2	99.87	99.73	99.86
3	99.91	99.75	99.86
4	99.87	99.73	99.86
Means	99.89	99.73	99.86

Corrections: Add 0.04 to the mean reading with the quartz plate and the white telescope. Add 0.08 to the mean reading of the yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.93
" " yellow light	99.81
" " white light	99.90
Mean of the means	99.88

READINGS AT 25°.

Five solutions were examined on the afternoon of April 12, at a temperature of 25°. This temperature and those following were obtained by artificial heat, the air in the observation room being kept in constant motion by means of electric fans. Every part of the room was thus kept at the same temperature.

	°V.
Mean reading of right-handed plate, white light	100.30
Mean reading of right-handed plate, yellow light	100.28
Mean reading of right-handed and left-handed quartz	8.46

Difference to be added, 91.82.

	Readings of solutions with quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.68	99.60	99.63
2	99.72	99.60	99.73
3	99.72	99.60	99.70
4	99.76	99.61	99.71
5	99.73	99.61	99.71
Means	99.72	99.60	99.70

Corrections: Add 0.06 to the reading with the quartz plate and the white light and 0.08 to the reading with the yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.78
" " yellow light	99.68
" " white light	99.76
Mean of the means	99.74

READINGS AT 30°.

On the afternoon of April 13, observations were made at 30°. The mean results of the readings were as follows:

	°V.
Right-handed quartz plate, white light	100.33
Right-handed quartz plate, yellow light	100.30
Right-handed and left-handed quartz plate, white light	8.50
The value of left-handed plate in terms of right-handed plate	91.83

	Reading of sugar solutions. Means of readings with quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.54	99.45	99.55
2	99.53	99.43	99.54
3	99.53	99.44	99.58
4	99.56	99.45	99.60
5	96.54	99.41	99.56
Means	99.54	99.44	99.57

Corrections: Add 0.03 to the readings of the quartz plate and white light, and 0.06 to the mean reading with yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.57
" " yellow light	99.50
" " white light	99.60
Mean of the means	99.56

Variation from the mean reading at 25°, 0.18.

READINGS AT 35°.

On the afternoon of April 14, a series of readings was made at 35°. The preliminary readings were as follows:

	°V.
Right-handed quartz plate, white light	100.33
Right-handed plate, yellow light	100.30
Right and left plates, white light	8.50
Difference in plates	91.83

	Readings of sugar solutions with		
	quartz plates. °V.	yellow light. °V.	white light. °V.
1	99.38	99.34	99.38
2	99.42	99.33	99.40
3	99.38	99.33	99.39
4	99.41	99.31	99.41
5	99.39	99.36	99.40
Means	99.40	99.33	99.40

Corrections: Add 0.03 to the mean reading with the quartz plate and that with the white light, and 0.06 to that with the yellow light.

	Corrected Means. °V.
Solutions, with quartz plate	99.43
" " yellow light	99.39
" " white light	99.43
Mean of corrected means	99.42

READINGS AT 40.°

On April 15, a series of readings was made at 40° with the following results:

	°V.
Right-handed plate, white light	100.35
Right-handed plate, yellow light	100.31
Right and left plates, white light	8.55
Difference between the two plates	91.80

	Readings of sugar solutions with		
	quartz plate. °V.	yellow light. °V.	white light. °V.
1	99.23	99.18	99.26
2	99.14	99.14	99.21
3	99.20	99.20	99.23
4	99.23	99.18	99.28
Means	99.20	99.18	99.25

Corrections: Add 0.01 to the readings with the quartz plate and white light, and 0.05 to the readings with yellow light.

	Corrected means. °V.
Solutions, with quartz plate	99.21
" " yellow light	99.23
" " white light	99.26
Mean	99.23

SUMMARY OF MEAN POLARIZATIONS FROM 4° TO 40°.

Temperature. Degrees.	Mean polarization. °V.	Differences. °V.
4	100.36	
10	100.20	0.16
15	100.06	0.14
20	99.88	0.18
25	99.74	0.14
30	99.56	0.18
35	99.42	0.14
40	99.23	0.18

The relations of the data given in this table are best shown by plotting them on cross-section paper. It is seen by this plot, which is appended hereto, that the line intersecting the different points determined by the instrument is practically a straight one. By plotting the line upon cross-section paper, therefore, it is easy to compute the variations for each degree or a fraction of a degree for a sugar polarizing practically 100° in the ordinary conditions secured in the use of the triple-shadow instrument with the Ventzke scale. For sugars of different content of sucrose the magnitude of the corrections to be employed is easily calculated and, for convenience, these corrections are given in the appended table for temperatures from 4° to 40° and for sugar content from 80 to 100 per cent. These data are computed from the points of intersection of the straight line showing the polarization of pure sugar measured by quartz wedges at temperatures from 0° to 40°. These data in extreme cases do not differ more than 0.03 from those determined from the direct observations made. While it is entirely probable that there are slight differences in the rates of change at different temperatures, as shown by the data of observation, for practical purposes, it is better to assume that the rate of change is uniform throughout and therefore is represented by a straight line.

Following is a table of corrections for polarizations made with quartz-wedge compensating polariscopes at temperatures other than the standard temperature of 17.5° C. To obtain the proper correction select the number found at the intersection of the horizontal column corresponding most nearly with the observed polarization, and the vertical column headed with the temperature at which the observation is made. This correction is to be subtracted from the observed polarization when the temperature is below 17.5° C., and added when the temperature of observation is above 17.5° C.

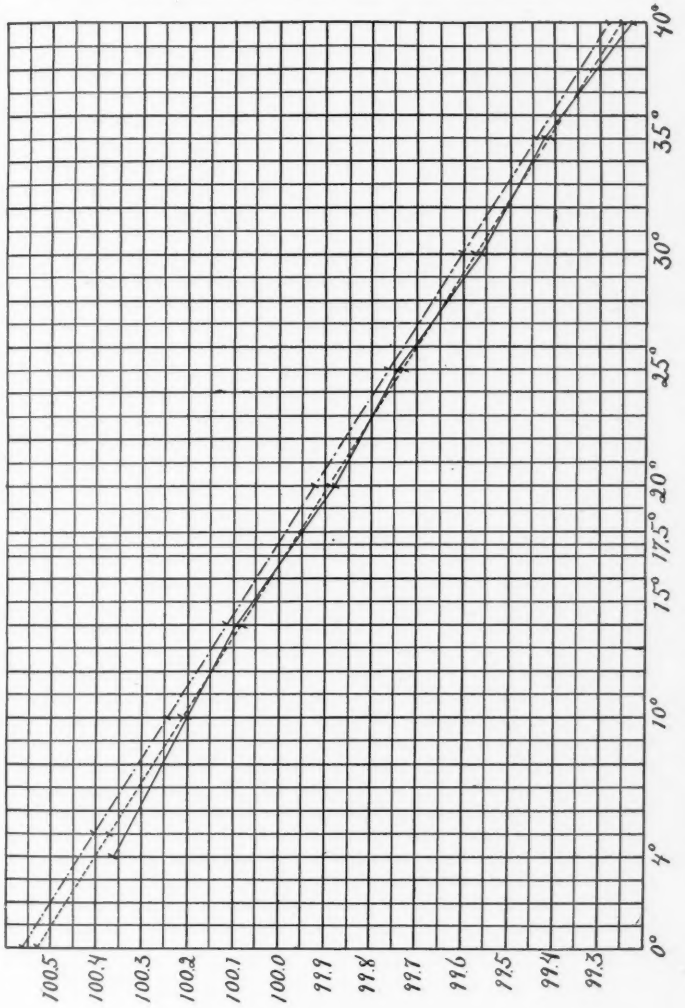
TEMPERATURE, DEGREES CENTIGRADE.

Degrees Ventzke.	4	5	6	7	8	9	10	11	12	13	14	15	16	17	17.5	18	19	20	21
100..	0.43	0.40	0.37	0.34	0.30	0.27	0.24	0.21	0.18	0.14	0.11	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.11
99..	0.43	0.40	0.37	0.34	0.30	0.27	0.24	0.21	0.18	0.14	0.11	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.11
98..	0.42	0.39	0.36	0.33	0.29	0.26	0.24	0.21	0.18	0.14	0.11	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.11
97..	0.42	0.39	0.36	0.33	0.29	0.26	0.23	0.20	0.17	0.14	0.11	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.11
96..	0.41	0.38	0.36	0.33	0.29	0.26	0.23	0.20	0.17	0.13	0.11	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.11
95..	0.41	0.38	0.35	0.32	0.29	0.26	0.23	0.20	0.17	0.13	0.10	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.10
94..	0.40	0.38	0.35	0.32	0.28	0.25	0.23	0.20	0.17	0.13	0.10	0.08	0.05	0.02	**0.00**	0.02	0.05	0.08	0.10
93..	0.40	0.37	0 34	0.32	0.28	0.25	0.22	0.20	0.17	0.13	0.10	0.07	0.05	0.01	**0.00**	0.01	0.05	0.07	0.10
92..	0.40	0.36	0.34	0.31	0.28	0.25	0.22	0.19	0.17	0.13	0.10	0.07	0.05	0.01	**0.00**	0.01	0.05	0.07	0.10
91..	0.39	0.36	0.34	0.31	0.27	0.25	0.22	0.19	0.16	0.13	0.10	0.07	0.05	0.01	**0.00**	0.01	0.05	0.07	0.10
90..	0.39	0.36	0.33	0.31	0.27	0.24	0.22	0.19	0.16	0.13	0.10	0.07	0.05	0.01	**0.00**	0.01	0.05	0.07	0.10
89..	0.38	0.36	0.33	0.30	0.27	0.24	0.21	0.19	0.16	0.12	0.10	0.07	0.05	0.01	**0.00**	0.01	0.05	0.07	0.10
88..	0.38	0.35	0.33	0.30	0.26	0.24	0.21	0.18	0.16	0.12	0.10	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.10
87..	0.37	0.35	0.32	0.30	0.26	0.23	0.21	0.18	0.16	0.12	0.10	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.10
86..	0.37	0.34	0.32	0.29	0.26	0.23	0.21	0.18	0.15	0.12	0.09	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.09
85..	0.37	0.34	0.31	0.29	0.26	0.23	0.20	0.18	0.15	0.12	0.09	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.09
84..	0.36	0.34	0.31	0.29	0.25	0.23	0.20	0.18	0.15	0.12	0.09	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.09
83..	0.36	0.33	0.31	0.28	0.25	0.22	0.20	0.17	0.15	0.12	0.09	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.09
82..	0.35	0.33	0.30	0.28	0.25	0.22	0.20	0.17	0.15	0.11	0.09	0.07	0.04	0.01	**0.00**	0.01	0.04	0.07	0.09
81..	0.35	0.32	0.30	0.28	0.24	0.22	0.19	0.17	0.15	0.11	0.09	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.09
80..	0.34	0.32	0.30	0.27	0.24	0.22	0.19	0.17	0.14	0.11	0.09	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.09
79..	0.34	0.32	0.29	0.27	0.24	0.21	0.19	0.17	0.14	0.11	0.09	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.09
78..	0.33	0.31	0.29	0.27	0.23	0.21	0.19	0.16	0.14	0.11	0.09	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.09
77..	0.33	0.31	0.28	0.26	0.23	0.21	0.18	0.16	0.14	0.11	0.09	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.09
76..	0.33	0.30	0.28	0.26	0.23	0.21	0.18	0.16	0.14	0.11	0.08	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.08
75..	0.32	0.30	0.28	0.26	0.23	0.20	0.18	0.16	0.14	0.11	0.08	0.06	0.04	0.01	**0.00**	0.01	0.04	0.06	0.08

TEMPERATURE, DEGREES CENTIGRADE—(*Continued*).

Degrees Ventzke.	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
100..	0.14	0.18	0.21	0.24	0.27	0.30	0.34	0.37	0.40	0.43	0.46	0.50	0.53	0.56	0.59	0.62	0.66	0.69	0.72
99..	0.14	0.18	0.21	0.24	0.27	0.30	0.34	0.37	0.40	0.43	0.46	0.50	0.52	0.55	0.58	0.61	0.65	0.68	0.71
98..	0.14	0.18	0.21	0.24	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.49	0.52	0.55	0.58	0.61	0.65	0.68	0.71
97..	0.14	0.17	0.20	0.23	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.49	0.51	0.54	0.57	0.60	0.64	0.67	0.70
96..	0.13	0.17	0.20	0.23	0.26	0.29	0.33	0.36	0.38	0.41	0.44	0.48	0.51	0.54	0.57	0.60	0.63	0.66	0.69
95..	0.13	0.17	0.20	0.23	0.26	0.29	0.32	0.35	0.38	0.41	0.44	0.48	0.50	0.53	0.56	0.59	0.63	0.66	0.68
94..	0.13	0.17	0.20	0.23	0.25	0.28	0.32	0.35	0.38	0.40	0.43	0.47	0.50	0.53	0.55	0.58	0.62	0.65	0.68
93..	0.13	0.17	0.20	0.22	0.25	0.28	0.32	0.34	0.37	0.40	0.43	0.47	0.49	0.52	0.55	0.58	0.61	0.64	0.67
92..	0.13	0.17	0.19	0.22	0.25	0.28	0.31	0.34	0.36	0.40	0.42	0.46	0.49	0.52	0.54	0.57	0.61	0.63	0.66
91..	0.13	0.16	0.19	0.22	0.25	0.27	0.31	0.34	0.36	0.39	0.42	0.46	0.48	0.51	0.54	0.56	0.60	0.63	0.66
90..	0.13	0.16	0.19	0.22	0.24	0.27	0.31	0.33	0.36	0.39	0.41	0.45	0.48	0.50	0.53	0.56	0.59	0.62	0.65
89..	0.12	0.16	0.19	0.21	0.24	0.27	0.30	0.33	0.36	0.38	0.41	0.45	0.47	0.50	0.53	0.55	0.59	0.61	0.64
88..	0.12	0.16	0.18	0.21	0.24	0.26	0.30	0.33	0.35	0.38	0.40	0.44	0.47	0.49	0.52	0.55	0.58	0.61	0.63
87..	0.12	0.16	0.18	0.21	0.23	0.26	0.30	0.32	0.35	0.37	0.40	0.44	0.46	0.48	0.51	0.54	0.57	0.60	0.63
86..	0.12	0.15	0.18	0.21	0.23	0.26	0.29	0.32	0.34	0.37	0.40	0.43	0.46	0.48	0.51	0.53	0.57	0.59	0.62
85..	0.12	0.15	0.18	0.20	0.23	0.26	0.29	0.31	0.34	0.37	0.39	0.43	0.45	0.48	0.50	0.53	0.56	0.59	0.61
84..	0.12	0.15	0.18	0.20	0.23	0.25	0.29	0.31	0.34	0.36	0.39	0.42	0.45	0.47	0.50	0.52	0.55	0.58	0.60
83..	0.12	0.15	0.17	0.20	0.22	0.25	0.28	0.31	0.33	0.36	0.38	0.42	0.44	0.46	0.49	0.51	0.55	0.57	0.60
82..	0.11	0.15	0.17	0.20	0.22	0.25	0.28	0.30	0.33	0.35	0.38	0.41	0.43	0.46	0.48	0.51	0.54	0.57	0.59
81..	0.11	0.15	0.17	0.19	0.22	0.24	0.28	0.30	0.32	0.35	0.37	0.41	0.43	0.45	0.48	0.50	0.53	0.56	0.58
80..	0.11	0.14	0.17	0.19	0.22	0.24	0.27	0.30	0.32	0.34	0.37	0.40	0.42	0.45	0.47	0.50	0.53	0.55	0.58
79..	0.11	0.14	0.17	0.19	0.21	0.24	0.27	0.29	0.32	0.34	0.36	0.40	0.42	0.44	0.47	0.49	0.52	0.55	0.57
78..	0.11	0.14	0.16	0.19	0.21	0.23	0.27	0.29	0.31	0.33	0.36	0.39	0.41	0.44	0.46	0.48	0.51	0.54	0.56
77..	0.11	0.14	0.16	0.18	0.21	0.23	0.26	0.28	0.31	0.33	0.35	0.39	0.41	0.43	0.45	0.48	0.51	0.53	0.55
76..	0.11	0.14	0.16	0.18	0.21	0.23	0.26	0.28	0.30	0.33	0.35	0.38	0.40	0.43	0.45	0.47	0.50	0.52	0.55
75..	0.11	0.14	0.16	0.18	0.20	0.23	0.26	0.28	0.30	0.32	0.34	0.38	0.40	0.42	0.44	0.47	0.50	0.52	0.54

GRAPHIC REPRESENTATION OF THE INFLUENCE OF TEMPERATURE ON THE ROTATION OF SUCROSE AS DETERMINED BY MEANS OF THE SCHMIDT AND HAENSCH TRIPLE-FIELD SACCHARIMETER.



The mean readings at the various temperatures of a commercial sugar, polarizing 99.97° Ventzke at 17.5° C., are shown by ————————.

The straight line from which the observations, made at temperatures from 10° C. to 40° C., inclusive, differ by only 0.01° Ventzke is shown by .....

The parallel straight line, representing the polarization of pure sucrose at temperatures from 0° to 40° C. is shown by —·—·—·—·—·—.

The total variation in polarization observed in this series of experiments for the 36° between 4° and 40° was 100.36—99.23, or 1.13° Ventzke, an average difference of 0.0314 for each degree of temperature. A comparison of this result with those of other observers is given in the following table:

Observer.	Variations in the polarization of a pure sugar for each degree centigrade. Degree Ventzke.
Andrews	0.0300
U. S. Coast and Geodetic Survey	0.0293
Schönrock and Landolt	0.0360
Wiley	0.0314
Mean	0.0317

DETERMINATION OF THE CHANGE IN POLARIZATION DUE TO THE INFLUENCE OF TEMPERATURE ON THE SPECIFIC ROTATION, OTHER TEMPERATURE INFLUENCES HAVING BEEN ELIMINATED.

Having thus determined with the greatest exactitude the total variations in polarizations under the influence of temperature, it remains to determine the magnitude of the deviation produced by temperature as a result of change of specific rotatory power of the sugar alone. It is evident that the temperature affects the polarization of a sugar solution in a compensating instrument in the following ways:

(1) By producing variations in the capacity of the flask; (2) by producing variations in the length of the observation tube; (3) by producing variations in the degree of concentration; (4) by changes produced in the rotating power of the compensating quartz wedges; and (5) by changes produced in the specific rotatory power of the sugar solution itself. It is understood that

the changes due to change of volume of the solution, are not considered here, because the readings are made at the same temperature as those at which the solutions are made.

It is evident, therefore, that if the magnitude of the first four of these factors can be determined, and the total variation in polarization corrected accordingly, the residual quantity of variation must be due to the influence of the temperature upon the specific rotatory power, and an effort will now be made to determine the magnitude of these various factors and to correct the total deviation from the polarization at 17.5° therefor.

(1) *Variations in the Size of the Flask.*—The flask employed in these investigations was most carefully graduated, both in this laboratory and by the Office of Weights and Measures of the Coast and Geodetic Survey, and was found to contain 100.23 cc. at a temperature of 17.5°. It was, therefore, a true Mohr flask, within 0.004 of a cubic centimeter. The variations in the size of the flask due to changes in temperature, calculated by the formula given in the tables of Landolt and Boernstein, are as follows:

Temperatures. °C.	Capacities. cc.	Capacities. Mohr cc.
4	100.196	99.966
10	100.211	99.981
15	100.224	99.994
17.5	100.230	100.000
20	100.236	100.006
25	100.249	100.019
30	100.261	100.031
35	100.274	100.044
40	100.286	100.056

(2) *Variations in the Length of the Tube.*—The glass observation tube employed in the investigations had a length of 200 mm. at a temperature of 17.5°. Its length at the other temperatures of observation is shown by the following table:

Temperature. °C.	Length. mm.
4	199.976
10	199.987
15	199.996
17.5	200.000
20	209.004
25	200.013
30	200.022
35	200.031
40	200.040

It is evident that the changes in the capacity of the flask and in the length of the tube are, to a certain extent, compensatory. As the flask increases in size, thus diminishing the proportion of the sugar to the volume, the tube increases in length, producing a partial compensation. The rate of increase in the capacity of the flask is, however, slightly greater than in the length of the tube, so that at temperatures varying considerably from 17.5° an appreciable correction is necessary. The amount of this correction is shown in the following table, which gives the variation in the first column of the length of the tube, in the capacity of the flask for each 5° in the second column.

Temperature. °C.	Variation in the length of tube. mm.	Variation in the capacity of flask. cc.
4	0.024	0.034
10	0.013	0.019
15	0.004	0.006
17.5	....	....
20	0.004	0.006
25	0.013	0.019
30	0.022	0.031
35	0.031	0.044
40	0.040	0.056

In the comparison of the variations in the capacity of the flask and the length of the tube due to temperature, it should be remembered that 100 cc. are compared with 200 mm. The percentage of variation, therefore, referred to units, is only half as great in the tube as in the flask. In other words, assuming that the capacity of the flask remains constant, it is seen that a variation of one-tenth mm. in the length of the tube produces a variation of only 0.05° in the polarization of the sugar. The variation in the length of the tube, therefore, expressed in millimeters, must be doubled in order to make a direct comparison. When this rule is applied it is seen that the correction for polarization, due to the volume of the flask, is directly proportional to the change in capacity. In other words, at 40° it is seen that the flask has increased 0.056 cc. in capacity. The polarization, therefore, as directly read on the instrument, should be increased by 0.056 to compensate for this increase in volume. On the other hand, we see that at the same temperature the length of the tube is increased by 0.040, and therefore the polarization

must be diminished by just half that amount to reduce it to the proper scale; namely, 0.020. Thus the total correction for the polarization at 40° for changes in the volume of the flask and length of the tube is made in the following way:

Example: Let the polarization at 40° be 99.24; add 0.056 to compensate for change in the volume of the flask and the polarization becomes 99.296. Subtract 0.020 to allow for the increase in the length of the tube, and the polarization becomes 99.276. Applying this principle to the correction of the polarizations obtained upon the standard samples of sugar at the different temperatures, we have the following for the polarizations of sugars for the temperatures named, after correction for changes induced by temperature in the volume of the flask and the length of the tube.

Temperature. °C.	Corrected polarizations. °V.
4	100.338
10	100.188
15	100.056
20	99.884
25	99.753
30	99.580
35	99.449
40	99.266

DERIVATION OF A FORMULA FOR COMPUTING THE CORRECTION FOR THE INCREASE IN THE CAPACITY OF THE FLASK AND FOR FOR THE INCREASE IN THE LENGTH OF THE TUBE WHEN THE OBSERVATION IS MADE AT ANY TEMPERATURE OTHER THAN THE STANDARD TEMPERATURE OF 17.5°.

Let the observed polarization at this temperature be 99.23° V; the capacity of the flask 100.056 Mohr cc. (1 Mohr cc. = 1.00234 true cc.); and the length of the tube 200.040 mm.

The number of grams of sugar per 100 cc. (Mohr) of the solution is

$$100.056 : 100 :: 26.048 : x$$

$$x = \frac{100 \times 26.048}{100.056} = 26.0334.$$

The true polarization of a solution containing x grams of sugar per 100 cc. (Mohr) and giving a reading of 99.23 is

$$x : 26.048 :: 99.23 : y.$$

Then the polarization corrected for the expansion of the flask,

$$y = \frac{26.048 \times 99.23 \times 100.056}{100 \times 26.048} = 99.286.$$

This value must now be corrected for the increased length of the tube, by the following ratios:

$$200.040 : 200 :: 99.286 : z.$$

Then the polarization corrected for the expansion of the flask and the tube is,

$$z = \frac{200 \times 99.286}{200.040} = 99.266.$$

Substituting the unreduced fractional value of y in the last proportion, we have:

$$200.040 : 200 :: \frac{26.048 \times 99.23 \times 100.056}{100 \times 26.048} : z.$$

$$z = \frac{200 \times 26.048 \times 99.23 \times 100.056}{200.040 \times 100 \times 26.048},$$

or dropping out the common factor 26.048, which occurs in both numerator and denominator, the expression becomes

$$z = \frac{200 \times 99.23 \times 100.056}{200.040 \times 100}.$$

If we let the capacity of the flask at 17.5° be represented by C; the capacity of the same flask at t degrees by C^t; the length of the tube at 17.5° by l; the length of the same tube at t degrees by l^t; and the polarization at t degrees by P^t; we have the following general formula:

P', the polarization corrected for expansion of the flask and observation tube $= \frac{lP^tC^t}{l^tC}$.

Example: A solution polarizes 100.360 under the following conditions:

$$t = 4° \text{ C.}$$
$$l = 200.$$
$$l^t = 199.976.$$
$$C = 100.$$
$$C^t = 99.966.$$

Then

$$P' = \frac{200 \times 100.36 \times 99.966}{199.976 \times 100} = 100.338.$$

VARIATION IN CONCENTRATION.

Perhaps there is no point connected with the polarization of sugars in which scientific literature contains more contradictory statements than that which relates to the influence of concentration on the specific rotatory power. It is not possible here to enter into a discussion of this subject, a matter which will be reserved later on for a separate investigation. It is sufficient here to call attention to the latest summary of our knowledge on this subject contained in Dr. Landolt's work entitled "Das optische Drehungsvermoegen, etc.," second edition, page 419. The conclusion which Landolt reaches from a study of the data at hand is as follows: "The specific rotatory power of sucrose for sodium light for all degrees of concentration below 30° may be taken as $[\alpha]_D^{17.5^\circ} = 65.5$." It is evident that the sugar with which the analytical data contained in this paper were obtained was practically pure, since under all the necessary conditions of polarization at 17.5° it gave a reading of 99.97. It is certain that the degree of concentration of the solutions changed with each degree at which the polarizations were made. For instance, in filling the flask at 4°, the quantity of water used was considerably greater by weight than when the flask was filled at 40°. The weight of sugar in all cases having remained the same, it is evident that the degree of concentration of the solution at 4° was considerably less than at 40°. Since, however, as we have just seen, there is practically no correction to be made for variations in concentration under 30 per cent., the influence of this slight difference in concentration may be absolutely eliminated from the calculation. It is established, therefore, that none of the variation noticed in polarization was due to differences in concentration.

CHANGES IN COMPENSATING POWERS OF THE QUARTZ WEDGES.

It is well known that the power of quartz, of a given thickness, of rotating a plane of polarized light, varies with the temperature. As the temperature rises the rotating power of the quartz increases. The rate of increase has been calculated by physicists, and the formula of Joubert is one which is

usually accepted for the purpose of determining the rotating values at different temperatures. This formula is

$$A_t = A_0 (1 + 0.000149t),$$

in which A_0 represents the rotating power of the quartz plate at a temperature of 0°, and A_t represents the rotatory power at any desired temperature. In this formula A may either represent degrees Ventzke or degrees of angular rotation.

E. Gumlich[1] has made careful determinations of the temperature coefficient of quartz for rays of different wave-lengths. He concludes that the influence of temperature on the rotatory power of quartz does not vary materially for light having wave-lengths varying from 656 $\mu\mu$ to 436 $\mu\mu$. For temperatures from 0° to 100° he expresses the influence of temperature on the specific rotatory power of quartz by the following equation $\phi' = \phi^0(1 + 0.000131t + 0.0000001951t^2)$.

Using this formula for calculating the value at 40° of a thickness of quartz which rotates 1° V. at 17.5° the value 1.00319 is obtained instead of 1.00335 as given in the table.

Substituting this value in the calculation of the mean corrected polarization obtained at 40° and in the calculation of the specific rotatory power of sucrose at 40°, the numbers 99.582 and 66.288 are obtained, respectively. The former number differs by 0.016° V. from the one given in the table, while the value for $[\alpha]_D^{40}$ is 0.011 less than the result previously noted. It is therefore evident that the use of the formula of Gumlich would not materially change the results reported in this paper.

Applying Joubert's formula to the investigation in question, we have the following data:

A thickness of quartz, which gives a rotation of 1° V. at 17.5°, produces at other temperatures the amount of rotation shown in the following table:

Temperature. °C.	Rotation. °V.	Difference from 17.5°
4	0.99799	0.00201
10	0.99888	0.00112
15	0.99963	0.00037
17.5	1.00000	0.00000
20	1.00037	0.00037
25	1.00112	0.00112
30	1.00186	0.00186
35	1.00261	0.00261
40	1.00335	0.00335

[1] Wiedemann's *Ann. phys. Chem.*, 59, 333; *Ztschr. des Vereins der deutschen Zuckerind.*, (*1898*), 11, 971–992.

If the compensating system of a polariscope be warmed to 40° C., the quartz wedge used in its construction rotates 1.00335 times the number of degrees Ventzke shown by a quartz of equal thickness at 17.5°.

The true polarization of a sugar solution which reads 99.266° V. at 40° C. (correction having been made for the change in the volume of the flask and in the length of the observation tube, due to change of temperature), is 99.266 × 1.00335, or 99.598° V.

Correcting all the results given on page 587, we have:

POLARIZATION OF THE SUGAR UNDER EXAMINATION AT TEMPERATURES FROM 4° TO 40° C.

(Corrections having been made for the changes caused by temperature in the volume of the flask, in the length of the observation tube and in the rotatory power of the quartz used in the construction of the instrument.)

Temperature. °C.	Polarization. ° V.
4	100.136
10	100.075
15	100.019
17.5	99.970
20	99.921
25	99.864
30	99.765
35	99.708
40	99.598

If the polarization at t degrees of a thickness of quartz which reads 1° V. at 17.5°, be designated by Q^t, we may extend the formula for P' given above, as follows:

P', the polarization in degrees Ventzke, corrected for changes due to temperature in the volume of the flask, in the length of the observation tube and in the rotatory power of the quartz of the compensating system of the instrument,

$$= \frac{lP^tC^tQ^t}{l^tC}; \text{ in which}$$

l = length of the observation tube at 17.5° C.

l^t = " " " " " " the temperature of observation.

C^t = capacity of the flask at the temperature of observation.

Q^t = polarization at t° of a thickness of quartz reading 1° V. at 17.5°.

P^t = observed polarization, degrees Ventzke.

C = capacity of the flask at 17.5° C.

Example:

$$\text{Let } t = 40^\circ.$$
$$P^t = 99.24.$$
$$l^t = 200.040.$$
$$C^t = 100.056.$$
$$Q^t = 1.00335.$$
$$l = 200.$$
$$C = 100.$$
$$P' = \frac{200 \times 99.23 \times 100.056 \times 1.00335}{200.040 \times 100} = 99.598.$$

It is evident, from an inspection of the above data, that a less thickness of the quartz wedge is required to compensate for the rotation produced in the plane of polarized light by a sugar solution at a higher than at a lower temperature. The result of this is that the apparent reading of the solution is lower than the true reading as the temperature of the quartz wedge and its rotating power increase.

CHANGES DUE TO PRESSURE ON THE QUARTZ PLATES AND WEDGES.

It is well known that any strain or pressure exerted on a piece of quartz will change its rotating power. Hence the operator must assure himself that he is using an instrument in which the rotating power of the quartz wedges and quartz plates is not changed by pressure due to changes in temperature. In the double compensating polariscope, used in these investigations, there are four quartz wedges, with independent settings. Theoretically the reading of a quartz plate mounted in such a way as to undergo no pressure, due to changes of temperature, by four quartz wedges, all independently mounted in the same way, should be practically the same at all temperatures. The permissible variations are due only to displacement of the zero mark, which is very common in double compensating instruments, to the personal errors of reading, which may amount to 0.10° V. and to changes in the nature or intensity of light.

The doctrine of probabilities would practically preclude the occurrence of a state of affairs in which the pressure exerted on a mounted quartz plate would be exactly compensated for by the sum of the pressures exerted on four independently mounted quartz wedges.

If in these conditions the readings of a quartz plate at widely varying temperatures in a double compensating instrument, agree within the limits of error above pointed out, it is a convincing proof, that neither the plate nor the wedges have suffered any change in rotating power due to pressure.

I will now compare the readings of the urnormal quartz plate used for control in these investigations, at the various temperatures employed, excluding those made at 4°, in which a different light was used.

READING OF URNORMAL QUARTZ PLATE AT DIFFERENT TEMPERATURES.

Temperature. °C.	Reading. °V.	Difference.
10	100.33	...
15	100.33	0.00
20	100.32	0.01
25	100.30	0.02
30	100.33	0.03
35	100.33	0.00
40	100.35	0.02

The remarkable uniformity of the readings of the urnormal plate, at such widely varying temperatures, proves beyond any reasonable doubt that none of the data obtained was influenced in any way by pressure exerted either on the quartz plate or wedges.

We find, therefore, the total difference due alone to change in specific rotatory power for 36° equal to 0.538° V., and for 1° 0.01494° V. It therefore appears that for each change of one degree in the temperature the polarization of a pure sugar on an instrument with a Ventzke scale suffers a change of 0.01494°, due exclusively to the change in the specific rotatory power of the sugar solution. Converting this into angular degrees by multiplying by the factor 0.3462, we get the magnitude of the change in specific rotatory power in angular measure due to each degree of change of temperature = 0.005172. It is now possible to convert the readings obtained on the Ventzke scale into angular measurement and to compute the specific rotatory power for each of the temperatures at which the observations were made. These calculations have been made and the results are found in the following table :

SPECIFIC ROTATORY POWER OF SUCROSE AT TEMPERATURES RANGING FROM 4° TO 40° C.[1]

Temperature of observation. °C.	Readings on Ventzke Scale.[2] °V.	Equivalent angular degrees with sodium light.	$[a]^t_D$	Differences. Range of temperature. °C.	Differences. For whole range.	Differences. For 1° C.
4	100.136	34.667	66.657	4 to 10	0.040	0.00667
10	100.075	34.646	66.617	10 " 15	0.038	0.00760
15	100.019	34.627	66.579	....	....	....
17.5	99.970	34.610	66.547	15 " 20	0.065	0.01300
20	99.921	34.593	66.514	20 " 25	0.038	0.00760
25	99.864	34.573	66.476	25 " 30	0.066	0.01320
30	99.765	34.539	66.410	30 " 35	0.038	0.00760
35	99.708	34.519	66.372	35 " 40	0.073	0.01460
40	99.598	34.481	66.299	....	....	....

This weight of sugar in 100.23 true cc. is equivalent to 26.004 grams (weighed *in vacuo*) in 100 true cc.

The formula for specific rotatory power is

$$[a]^t_D = \frac{100\,a}{lc}.$$

$$[a]^t_D = \frac{100\,a}{2 \times 26.004} = aC, \text{ when } C = \text{the constant, } \frac{100}{2 \times 26.004}.$$

The specific rotatory power for a given temperature may be calculated directly from the reading of the saccharimeter at the given temperature by the use of the following formula:

$$[a]^t_D = \frac{0.3462\,P^t V^t Q^t}{26.0639\,l^t}.$$

0.3462 = the value in angular degrees of 1° V.

P^t = the observed polarization, degrees Ventzke.

V^t = the capacity of the flask at the temperature of the observation, expressed in true cc.

Q^t = the value in degrees Ventzke at $t°$ of the thickness of quartz which gives a rotation of 1° V. at 17.5° C.

l^t = the length of the observation tube in decimeters at the temperature of the observation.

26.0639 = the weight in grams (weighed in vacuo) of sugar contained in the quantity of the solution prepared.

[1] The observations were made with a triple-field saccharimeter, the readings being converted to angular degrees by use of the factor 0.3462. The concentration was 26.004 grams (weighed *in vacuo*) sugar in 100 true cc. (26.048 grams weighed in air in 100 Mohr cc).

[2] Corrected for all variations except in specific rotation.

Example: A solution of 26.048 grams of sugar (weighed in air) prepared at 40° C. in a flask that holds 100.23 true cc. at 17.5° C., polarizes 99.23° V. at 40° C.

This solution contains 26.0639 grams of sugar (weighed in vacuo).

	log 0.3462	= 9.5393271
log P^t =	log 99.23	= 1.9966430
log V^t =	log 100.286	= 2.0012403
log Q^t =	log 1.00335	= 0.0014525
	colog 26.0639	= 8.5839606
colog l^t =	colog 2.0004	= 9.6988832
	log $[\alpha]_D^{40}$	= 1.8215067
	$[\alpha]_D^{40}$	= 66.299°

From the foregoing data it is seen that the temperature has a marked effect upon the specific rotatory power of sucrose. After having obtained a large number of readings on a most delicate polariscope in which the conditions of temperature were most carefully controlled, it has been possible to estimate the magnitude of this change in rotatory power. It is seen that the specific rotatory power of the sugar employed at 17.5° is 66.547, and at the extreme ranges of temperature which were reached in the investigation, we find that the specific rotatory power at 4° of the same sugar is 66.657, and at 40°, 66.299. It is thus seen that the specific rotatory power of the sucrose solution increases as the temperature falls, and decreases as the temperature rises, and the mean magnitude of the variation for each degree is 0.00994.

A comparison of this result with those of other observers is given in the following table:

Observer.	Mean changes in the specific rotatory power of sucrose per °C.
Andrews	0.01140
Schönrock	0.01440
Wiley	0.00994
Mean	0.01191

It appears from the results of the investigation that the mean rate of increase is not the same at every temperature, as for instance, it appears to be greater from 15° to 17.5°, from 20°

to 25°, and from 30° to 35° than it is at the other points at which the observations were made. Numerous series of observations, however, would be necessary, on account of the small magnitudes involved, to definitely determine this question.

My thanks are due to Mr. W. H. Krug, who assisted me in obtaining all the experimental data given in this paper, and who cheerfully endured the fatigue and discomfort of working for several nights at very low temperatures; to Mr. E. E. Ewell, who assisted in calculating the data and in constructing the graphical charts and tables of correction; and to Mr. G. L. Spencer, who independently determined the values of the urnormal quartz plates used in controlling the polarizations.

THE DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC SUBSTANCES CONTAINING NITROGEN.

BY O. F. TOWER.

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IN determining carbon and hydrogen in substances containing nitrogen, use is commonly made of a metallic copper spiral at the exit end of the combustion tube to reduce oxides of nitrogen. Liebig was the first to observe that such oxides might be formed, and he showed that the amount of nitric oxide formed, when determining nitrogen by heating with copper oxide, was sufficient to vitiate the results.[1] He further showed that no appreciable quantities of other oxides of nitrogen could be formed, for when the quantity of nitrogen collected was increased by the amount of nitrogen in the nitric oxide produced, the correct percentage of nitrogen in the substance was obtained. Later Klingemann[2] determined the amount of nitric oxide formed from a variety of complex nitrogen-containing substances, when nitrogen is determined by burning with copper oxide according to the method of Frankland and Armstrong. His results show that the quantity of nitric oxide produced is usually very small, from 0.00 to 0.28 cc., occasionally it is more, and in the case of picric acid 0.90 cc. was found. This last equals only 0.0011 gram. The amount of the substance burned was commonly about 0.1 gram. His results show further that the amount of

[1] Pogg. *Ann.*, **18**, 357.
[2] *Ber. d. chem. Ges.*, **22**, 3064.

nitric oxide formed does not depend on the nature of the substance, nor on the percentage of nitrogen in the substance, and, moreover, it is very variable for different combustions of the same substance. It, however, seems to be somewhat influenced by the rapidity of the combustion. No direct determinations of the amount of nitrogen oxidized seems to have been made in connection with the determination of carbon and hydrogen in substances containing nitrogen. A few combustions of such substances, made at the time work on a former article[1] was in progress, seemed to show that no appreciable quantities of oxides of nitrogen could be formed, and that, consequently, a metallic copper spiral was unnecessary, particularly in the case of those substances where the nitrogen was in the amidic form. The following work was, therefore, undertaken to determine, if possible, if oxides of nitrogen are formed in such quantity as to interfere with the accuracy of the determinations of carbon and hydrogen, rendering imperative the use of a metallic copper spiral when burning all such compounds.

The method of making combustions differed somewhat from that described in the article just cited. No cylinder of compressed oxygen was at my disposal in this laboratory, so that it was necessary to use oxygen prepared in the usual manner and confined in a gas-holder over water. For reasons which will be given later, at the close of most of the combustions the oxygen was swept out by air. The series of absorbing tubes was changed slightly by introducing after the first soda-lime tube a small U-tube containing glass wool drenched with sulphuric acid instead of the tube containing in one side soda-lime and in the other calcium chloride. This change was made for the reason that occasionally a carbon determination came out low. It has been shown by Dibbits[2] that calcium chloride at ordinary temperature fails to absorb about eight per cent. of the water vapor necessary to saturate the air at the same temperature. In cases where combustions are carried on in an atmosphere of oxygen, so that only a small quantity of gas, comparatively, is aspirated through the system of tubes, the error thus caused is usually small enough to be inappreciable. Where, however, the oxy-

[1] This Journal, 21, 389.

[2] *Ztschr. anal. Chem.*, 15, 148.

gen is afterwards displaced by air, and consequently the quantity of gas which passes through the system is much greater, a considerable error can result. With this arrangement of tubes there was no certain means of telling when the absorptive power of the soda-lime tube was exhausted. Hence no soda-lime tube was used for more than two combustions.

The substances burned were selected so as to represent different types of bodies containing nitrogen. They were hippuric acid, paratoluidine, urea, dinitrobenzene, nitraniline, and picric acid. Among these are compounds containing amido and nitro groups, some having a large and some a small percentage of nitrogen. The results obtained with the first five will be given first, and afterwards picric acid will be discussed by itself. Only well-crystallized samples of these preparations were employed. Their purity was established by determining the percentage of nitrogen which they contained. All nitrogen determinations were made according to the Kjeldahl method modified to include the nitrogen of nitrates, as adopted by the Association of Official Agricultural Chemists.[1] The determinations were made in duplicate and resulted as follows:

Substance.	Nitrogen. Found. 1.	Found. 2.	Theoretical.
	Per cent.	Per cent.	Per cent.
Hippuric acid	7.85	7.82	7.82
Paratoluidine	13.05	13.19	13.08
Urea	46.58	46.69	46.67
Dinitrobenzene	16.62	16.65	16.67
Nitraniline	20.33	20.28	20.29

The agreement between the results obtained and the theoretical is such as to show that the substances were sufficiently pure.

The carbon and hydrogen in these compounds was then determined, sometimes using and sometimes without using a copper spiral. If oxides of nitrogen were formed, and no copper spiral were used, these oxides would pass over and, with the exception of nitric oxide, be absorbed in great part by the concentrated sulphuric acid, thereby increasing the apparent weight of absorbed water, and the corresponding percentage of hydrogen. In the first few combustions, in fact, the percentage of hydrogen

[1] Methods of Analysis, Bulletin 46, Division of Chemistry, U. S. Department of Agriculture, p. 17.

was too high, whether or not a copper spiral were used. For example, from the combustion of dinitrobenzene, the following percentages of hydrogen were obtained :

	Per cent.
With copper spiral	2.84
" " "	2.62
" " "	2.66
Without copper spiral	2.69
" " "	2.54
" " "	2.75
Theoretical	2.38

The inference from these results seemed to be that something rendered the copper spiral ineffective. At the beginning of each of these combustions the tube was filled with oxygen gas, and it was noticed that when a metallic copper spiral was introduced, as it became heated it was immediately oxidized. It is possible that the oxidation was so complete as to prevent the copper having any reducing effect on oxides of nitrogen. To obviate this, at the close of each combustion the oxygen in the tube was swept out by air in the usual manner. With this precaution it could easily be observed that the copper spiral was not oxidized so rapidly as before. The percentage of hydrogen was, however, still too high, varying little from the former results.

In all these combustions the percentage of carbon found was constant and agreed well with the theory. Blank tests at this time showed that the drying train was inadequate, admitting water into the combustion tube. Nothing, therefore, could be inferred from the foregoing results. The sulphuric acid in the drying cylinders was replenished and the number of cylinders increased to three. No further difficulty was then experienced in freeing the entering gases from water. Further combustions now gave a lower percentage of hydrogen, but in the case of substances containing very little hydrogen the results were still somewhat higher than the theory ; no higher, however, than is frequently the case in elementary analysis of compounds of this kind. The results are given below. To avoid the possibility of the copper spiral becoming immediately oxidized and thus proving ineffective, the oxygen was in every case swept out with air.

Substance.	Copper spiral.	Amount used.	Amount CO_2 found.	Carbon Found.	Carbon Theor.	Amount H_2O found.	Hydrogen Found.	Hydrogen Theor.
		Gram.	Gram.	Per cent.	Per cent.	Gram.	Per cent.	Per cent.
Hippuric acid..	with	0.2017	0.4464	60.37	60.34	0.0915	5.08	5.03
	"	0.2057	0.4558	60.31	....	0.0937	5.10	...
	without	0.1895	0.4176	60.11	....	0.0860	5.08	...
	"	0.2045	0.4521	60.30	....	0.0937	5.13	...
	"	0.2032	0.4485	60.21	....	0.0930	5.12	...
Paratoluidine .	without	0.1912	0.5498	78.44	78.50	0.1452	8.50	8.41
	"	0.1821	0.5242	78.52	....	0.1369	8.41	..
Urea.....	with	0.2011	0.1472	19.97	20.00	0.1210	6.73	6.67
	"	0.2031	0.1490	20.01	....	0.1243	6.85	...
	"	0.2119	0.1565	20.15	....	0.1291	6.82	...
	without	0.2028	0.1487	20.00	....	0.1240	6.84	...
	"	0.2116	0.1560	20.11	....	0.1288	6.81	...
	"	0.2006	0.1471	20.00	....	0.1204	6.72	...
	"	0.2052	0.1498	19.91	....	0.1245	6.79	...
Dinitrobenzene.	with	0.2194	0.3444	42.82	42.86	0.0482	2.46	2.38
	"	0.2200	0.3467	42.98	....	0.0496	2.42	...
	without	0.2161	0.3400	42.92	....	0.0486	2.52	...
	"	0.2108	0.3311	42.84	....	0.0446	2.37	...
Nitraniline	"	0.1750	0.3348	52.19	52.17	0.0702	4.49	4.35
	"	0.1782	0.3412	52.23	....	0.0701	4.40	...

On comparing the results with and without the use of a copper spiral, there is no ground for assuming the formation of oxides of nitrogen. These results were not, however, considered sufficient proof that no such oxides are formed.

As was stated before, any such oxides, with the exception of nitric oxide,[1] would be retained by concentrated sulphuric acid. The sulphuric acid in the first U-tube was, therefore, examined for nitrogen by the Kjeldahl process. The solution of hydrochloric acid used in this work was approximately seminormal, ten cc. containing 0.1845 gram pure acid. The standard ammonia solution was about one-sixth the strength of the acid, ten cc. being equivalent to 0.01200 gram nitrogen. The ammonia solution gradually became weaker on standing, so that its strength in terms of the standard acid was determined each day it was used. Blank determinations were first made to see if the reagents employed were free from nitrogen. Four cc. hydrochloric acid were used in each determination, and the titrations with ammonia were 23.30, 23.18, 23.10, and 23.26 cc., respect-

[1] Nitric oxide is not absorbed by concentrated sulphuric acid. See *J. Soc. Chem. Ind.*, *1885*, 178; *Ber. d. chem. Ges.*, **18**, 1391; *Chem. News*, **55**, 28.

ively, average 23.21 cc. Had the reagents contained no nitrogen, the quantity of ammonia required in each case would be 23.70 cc., which differs from the average by 0.49, or in round numbers 0.50 cc., equivalent to 0.0006 gram nitrogen. Allowance was made for this in all the following determinations. The sensitiveness of the method can also be seen from the above figures. The greatest difference between any two titrations is 0.20 cc., equivalent to 0.00024 gram nitrogen, and the greatest variation from the average is 0.11 cc., equivalent to 0.00013 gram nitrogen. By this method, therefore, nitrogen can be determined within 0.0002 gram. This is sufficiently accurate for this work, as the limit of error in weighing a U-tube under changing atmospheric conditions is usually not less than 0.0002 gram. Simple U-tubes were used to absorb the water and not those of the Volhard pattern with a bulb on one arm, as it was desired that all water should be taken up directly by the sulphuric acid. The U-tubes were filled with some of the same acid as that used for the Kjeldahl determinations. After a combustion the contents of these tubes were poured into a digestion flask, and the tubes well rinsed with additional sulphuric acid. The amount of nitrogen in the acid was then determined.

The sulphuric acid used to absorb the water in most of the combustions, whose results are given in the last table, was treated thus, but no traces of nitrogen could be found. This was surprising, for it was confidently expected that not negligible quantities of nitrogen were oxidized, particularly in the case of nitro bodies, as nitraniline and dinitrobenzene. Several combustions were then made with these two substances, using the same sulphuric acid to absorb the water from two, and sometimes from three, separate combustions. This acid was then examined for nitrogen, but none was found. Soda-lime will absorb all oxides of nitrogen except perhaps nitric oxide.[1] If, therefore, any of the other oxides of nitrogen should escape absorption by the sulphuric acid, they would certainly be absorbed by the soda-lime. The soda-lime which had been used in several combustions of nitraniline and dinitrobenzene was, consequently, treated with concentrated sulphuric acid in a flask,

[1] Nitric oxide is not absorbed by strong alkalies. See *J. Chem. Soc.*, (1877), **2**, 37; Wien: *Monatshefte*, **13**, 86.

and the mixture distilled until sulphuric acid commenced to come over. This distillate was examined for nitrogen, but none was found. The results of all these determinations were very similar to those obtained in the blank tests. An example will suffice.

SUBSTANCE BURNED, DINITROBENZENE.

	cc.
Hydrochloric acid used in each case	3.00
Theoretical amount of ammonia to neutralize, allowance being made for nitrogen in reagents	17.40
Actual amount of ammonia used in each titration (substance examined for nitrogen):	
Sulphuric acid from one combustion	17.48
" " " two combustions	17.37
" " " three combustions	17.50
Distillate from soda-lime, two combustions	17.42

In other cases titrations were obtained running from 17.32 to 17.50 cc., the former being the lowest figure ever observed, so that it is safe to draw the inference, that no appreciable quantities of oxides of nitrogen which are absorbed either by concentrated sulphuric acid or soda-lime were formed.

Small quantities of nitric oxide may have been formed, as this gas would pass the sulphuric acid and soda-lime without being absorbed, and consequently would not affect the determinations of carbon and hydrogen. Of course, if it came in contact with oxygen in the tube, it would immediately become oxidized, and then could be readily absorbed. In making a combustion there was, however, little opportunity for oxidation. At the beginning of a combustion the tube was full of air. During the preliminary heating of the substance no air or oxygen was aspirated through the system, so that the oxygen of the contained air would very soon either be used up or driven out by the production of carbon dioxide and other gases. Only after the substance was completely charred and there was no further bubbling of gas through the sulphuric acid of the water-absorbing tube, was the aspiration of oxygen commenced. From Klingemann's results it would be inferred that some nitric oxide might be formed, but in any event very little. It may be remarked that no red fumes were ever noticed where the unabsorbed gases

finally escaped into the air, although under somewhat different circumstances such fumes have been observed by others.[1]

The results with picric acid will now be given. With this substance Klingemann[2] obtained much more nitric oxide than with any other substance which he used.

DETERMINATION OF CARBON AND HYDROGEN IN PICRIC ACID.

Theoretical values, carbon 31.44 per cent., hydrogen 1.31 per cent.

Combustion number.	Copper spiral.	Amount used.	Amount carbon dioxide found.	Corresponding carbon.	Amount water found.	Corresponding hydrogen.
		Gram.	Gram.	Per cent.	Gram.	Per cent.
1	with	0.1551	0.1793	31.53	0.0208	1.50
2	"	0.1551	0.1786	31.41	0.0201	1.45
3	without	0.1605	0.1875	31.86	0.0250	1.75
4	"	0.1613	0.1894	32.03	0.0266	1.85
5	"	0.1512	0.1771	31.95	0.0210	1.55
6	"	0.1614	0.1881	31.79	0.0244	1.69
7	"	0.1595	0.1866	31.91	0.0229	1.61

DETERMINATION OF NITROGEN IN THE SULPHURIC ACID AND SODA-LIME USED IN THE PREVIOUS COMBUSTIONS.

Hydrochloric acid used each time 3.00 cc., equivalent to 17.40 cc. ammonia.[3]

Combustion number.	Sulphuric acid. Titration.	Difference.	Nitrogen.	Soda-lime distillate. Titration.	Difference.	Nitrogen.
	cc.	cc.	Gram.	cc.	cc.	Gram.
2	17.35	...	....	17.42	...	....
3	16.85	0.55	0.0007	17.05	0.35	0.0004
4	16.30	1.10	0.0013	16.75	0.65	0.0008
5	17.25	0.15	0.0002	16.90	0.50	0.0006
6	17.20	0.20	0.0002	16.55	0.85	0.0010
7	17.22	0.18	0.0002			

From the first table it will be seen that the results, when no copper spiral was used, not only in almost every case are higher than the results with the copper spiral, but they also do not agree so well with the theory. The second table shows that some nitrogen was found both in the sulphuric acid and in the soda-lime when no copper spiral was used, which proves that small quantities of one or more of the oxides of nitrogen were formed and absorbed by these reagents. The nitrogen determinations of combustion 1 were lost. There is, however, no reason to suppose they would have differed materially from those

[1] Zincke and Kegel: *Ber. d. chem. Ges.*, **23**, 246.

[2] 0.90 cc., equivalent to 0.0011 gram NO from about 0.1 gram picric acid. *Ber. d. chem. Ges.*, **22**, 3069.

[3] Allowing for nitrogen in reagents. In this table the columns headed "Difference" give the differences between 17.40 and the numbers in the columns immediately preceding.

of 2, which showed no nitrogen was present. In combustion 4, the substance was introduced while the tube was quite warm. Shortly after closing the tube a slight explosion took place. As the stoppers were not blown out, the combustion was completed. The explosion probably accounts for the larger amount of nitrogen found in this case. In 6 and 7, the same soda-lime was used for both. The amount of nitrogen obtained from it, therefore, resulted from two combustions.

To show whether or not these amounts of nitrogen account approximately for the high percentages of carbon and hydrogen when no copper spiral was used, these percentages have been recalculated in combustions 3, 4, and 5, on the hypothesis that the nitrogen was absorbed as nitrogen peroxide, NO_2. As will be observed, making this allowance causes the results to agree substantially with those when a copper spiral was used.

RECALCULATION OF PERCENTAGES OF CARBON AND HYDROGEN IN PICRIC ACID.

Combustion number.	NO_2 corresponding to N found in H_2SO_4.	Corrected hydrogen.	NO_2 corresponding to N found in soda-lime.	Corrected carbon.
	Gram.	Per cent.	Gram.	Per cent.
3	0.0020	1.60	0.0013	31.65
4	0.0040	1.57	0.0023	31.63
5	0.0006	1.51	0.0018	31.57

The effect of burning picric acid, using a copper boat, was tried with the hope that it would completely reduce any oxides of nitrogen. In some instances the picric acid was also mixed with powdered copper oxide. In every case, however, an explosion of considerable violence occurred, no matter how gradually the tube was heated, so that no results could be obtained.

To show that the Kjeldahl method is accurate for determining small amounts of nitrogen existing in the nitro condition, the results obtained from analyzing very small quantities of dinitrobenzene are given.

NITROGEN DETERMINATIONS WITH DINITROBENZENE.

Amount used.	Hydrochloric acid used.	Ammonia to neutralize, allowing for N in reagents.	Titration obtained.	Difference.	Corresponding nitrogen.	Theoretical nitrogen in substance taken.
Gram.	cc.	cc.	cc.	cc.	Gram.	Gram.
0.0100	3.00	17.40	16.05	1.35	0.00162	0.00167
0.0100	3.00	17.40	15.92	1.48	0.00177	0.00167
0.0050	3.00	17.40	16.80	0.60	0.00072	0.00083
0.0050	3.00	17.40	16.65	0.75	0.00090	0.00083

This shows conclusively that this method is well adapted to the purpose for which it has been used in this work.

The results of this investigation may be summed up as follows :

Amido compounds, of which urea, hippuric acid, and paratoluidine were taken as types, yield no oxides of nitrogen absorbed by concentrated sulphuric acid or by soda-lime. It is, therefore, not necessary to use a copper spiral when burning them.

Of the nitro substances burned, nitraniline, dinitrobenzene, and picric acid, only the last gave oxides absorbed by the reagents. Judging from the increase in weight of the absorbing tubes, the nitrogen was probably for the most part absorbed as nitrogen peroxide.

Nitric oxide may have been produced to a limited extent in any of the combustions. For, unless this oxide is further oxidized, it is not absorbed by either concentrated sulphuric acid or soda-lime, and consequently has no effect on the accuracy of the determination of carbon and hydrogen.

ADELBERT COLLEGE, CLEVELAND, O.

PARAFFIN AS AN ADULTERANT OF OLEOMARGARINE.[1]

BY JOSEPH F. GEISLER.

Received March 23, 1899.

ONE often hears of adulterated food, but rarely are such sophistications of a nature that they may be deemed injurious to health. The recent finding of paraffin as an adulterant in a number of samples of commercial oleomargarine may therefore prove of interest.

Though paraffin has been mentioned as an adulterant of chocolates and candies[2], the use of such an indigestible substance as an adulterant of oleomargarine seemed so improbable that the actual separation of the paraffin was required to convince some skeptical minds.

Its use in oleomargarine is by no means new, for I first observed it in a commercial sample in September, 1893, and reported the fact to the New York State Department of Agriculture. The general properties of the fat of the sample, its

[1] Read at the March meeting of the New York Section.

[2] U. S. Dispensatory, p. 1091.

behavior during saponification, and the abnormally low specific gravity 0.894 $\left(\text{at } \frac{100^\circ \text{ F.}}{\text{water } 100^\circ \text{ F.}}\right)$ indicated an irregularity and the probable presence of paraffin. Although the sample under examination amounted to only a few grams, sufficient of the unsaponifiable matter was obtained from the same to show that it was paraffin. It was impossible at the time to get more of this particular sample nor duplicates of several others in which paraffin was found between that date and March, 1894, when I was enabled to prepare an exhibit of the paraffin extracted from one of the samples. About this time experts of the Department of Agriculture, in the course of their inspections in New York and Brooklyn, found quite a number of samples of oleomargarine which, upon analysis, were found to contain paraffin. Some of these were analyzed by Drs. Love, Waller, Stillwell, and myself, and the amounts of paraffin in the various samples were found to range from 9.72 per cent. to 11.25 per cent.

The publicity given the matter at that time possibly caused a discontinuance of the use of paraffin in excessive quantities. At least I did not again observe any positive indications of paraffin in the customary analyses of any of the numerous samples examined until about six months ago and subsequently, when I found paraffin in five different samples which had been taken by the experts of the department in their regular inspections of grocery stores, restaurants, etc., in New York and Brooklyn. One of the samples, a one-pound print, and which had been sold for butter at twenty-two cents per pound, enabled me to make three exhibits of the extracted paraffin. The amounts of paraffin found in these samples ranged from 5 to 11.76 per cent.; in other words, from three to a little over six pounds per sixty-pound tub. The strip of paraffin extracted from commercial oleomargarine which I exhibit herewith, amounting to forty-three grains, is a little short of the amount actually contained in one ounce of one of these samples.

The extent of this character of adulteration it is almost impossible to determine, since much of the goods are sold secretly and in many instances palmed off for butter to unsuspecting purchasers and consumers. That much of the "oleo" in this market is sold under the guise of butter is evidenced by the tes-

timony of witnesses under oath in hundreds of cases prosecuted in the courts of this city during the past few years. The samples which the inspectors take represent only a small percentage of what goes into consumption. Finally, the samples in the hands of the chemist are, as a rule, not examined with a view of determining possible adulterants, but simply to ascertain whether the substance is butter or a butter substitute. In such examination two to three per cent. of paraffin would scarcely attract the attention of the analyst, while in exceptional cases even five per cent. might go unnoticed, as that quantity will dissolve clear in the alcoholic soap solution under the conditions of the Reichert method for butter analysis. Analysts who are not in the habit of taking the specific gravity of the fat, would in such instances be almost certain to overlook the adulterant.

The samples which would not saponify clear and which gave rise to suspicions on account of the abnormally low specific gravity of the fat, 0.9018 down to 0.8907 at 100° F. (water 100° F.) were the only ones specially examined for paraffin. The fat of one of these samples would not melt clear under 106°, and congealed at 105° F. The separated and purified paraffin from the same had a melting-point of 127°+. The photomicrographs shown herewith were prepared from the fat of this sample. The amorphous masses seen about the fat crystal are due to the presence of paraffin, and were particularly conspicuous in all the slides prepared from this sample. Plate 1 shows the microscopical appearance under polarized light with dark field (crossed Nicols), while in Plate 2 the field is illuminated, producing practically the reverse effect observed in Plate 1. Photomicrograph × 100 diam. The proportions of the Reichert method (two and five-tenths grams of fat to twenty cc. eighty per cent. alcohol containing one gram potassium hydroxide) may be used to advantage in testing for paraffin. The flask with a Liebig condenser attached should be shaken vigorously during the saponification, as this hastens and facilitates the same. After complete saponification, dilute the alcoholic soap solution with an equal volume of water. If two to three per cent. or over of paraffin is present, the solution will turn turbid and much of the separated paraffin can be collected by careful alternate heating and chilling the solution. Such separated matter must of course be examined

as to its identity. A soap solution remaining clear under the above conditions and dilutions would indicate that the fat was free from paraffin, or that it contains under three per cent.

It is pertinent to say that the object of the use of paraffin in oleomargarine is not to cheapen the article, but to make a more homogeneous fat mixture by preventing the separation of the fats and oils, and also to affect the general consistency and appearance of the mass and its behavior under the trier in sampling. One of these samples was with difficulty distinguished from butter by physical tests.

The use of paraffin under these conditions naturally gives rise to the query, What effect has it upon the system? I have been unable to find any records of researches as to the physiological effects of paraffins[1] which throw much light on the subject. Paraffin is generally regarded as an indigestible substance. This is undoubtedly true of paraffin taken into the system by itself. An interesting physiological question, however, presents itself in connection with the use of this substance in oleomargarine for the following reasons:

1. The paraffin is dissolved in the vegetable and animal fats constituting the oleaginous part of the compound.

2. The fat mixture in most cases melts at the normal temperature of the body.

3. The fat mixture is in a highly emulsified condition.

These conditions are so different from those presented in the occasional swallowing of small masses of paraffin that no analogies as to absorbability are presented from which to draw a fair inference. Hager[1] cautions against the internal use of paraffins. It would appear, however, that the symptoms there noted were caused by the lighter petroleums which at that time were commonly called paraffin, and thereby possibly misleading the translators. At the present time there are no data to warrant anyone in saying that the use of paraffin, as above, is harmless in its effects upon the system.

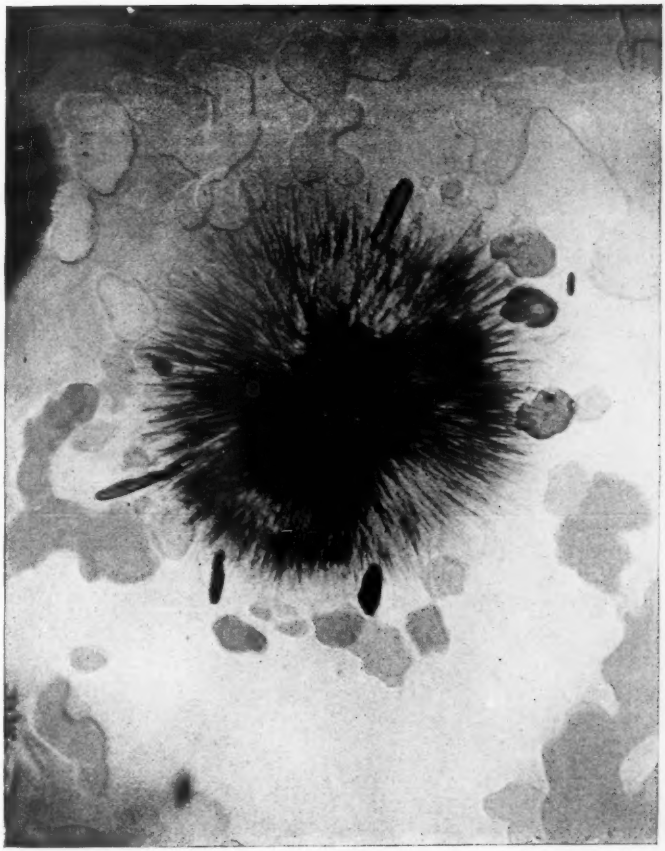
Although paraffin is an unsaponifiable substance, it is a question whether, under the above conditions, some of the paraffin is not absorbed in the system along with the other fats, and whether more serious disturbances may not arise than could be expected from the ordinary digestive disturbances attributable to the indigestibility of the greater part of the adulterant.

[1] Hager: *Pharm. Praxis*, Suppl., pp. 896, 899; *J. Pharm. Assoc.*, **34**, 309.

Photomicrograph × 100 diameters.

PLATE I.—ADULTERATED OLEOMARGARINE.

Exhibiting appearance of crystallized fat of commercial oleomargarine under microscope and polarized light with crossed Nicols. The white irregular masses are attributable to the presence of paraffin in the sample.



Photomicrograph × 100 diameters.

PLATE II.—ADULTERATED OLEOMARGARINE.

Same crystal as Plate I, but differently illuminated by polarized light and selenite and showing more conspicuously the amorphous masses of irregular shapes.

XANTHINE BASES IN SUGAR-CANE.

By Edmund C. Shorey.

Received April 3, 1899.

IF a sample of cane-juice be clarified in the ordinary way with lead subacetate, the excess of lead removed by sodium carbonate, or hydrogen sulphide, the solution made alkaline with sodium hydroxide, if not already so, a few drops of Fehling's solution added, and heated to boiling, a whitish precipitate is formed which rapidly becomes green. This was thought to indicate the presence of xanthine bodies. When solutions containing xanthine bases and reducing bodies are treated in this way with Fehling's solution, cuprous oxide is first formed by the action of the reducing bodies, and with this cuprous oxide the xanthine bases unite forming a greenish-white precipitate, Cu_2 combining with one molecule of the xanthine body. If the Fehling's solution be in excess, and there be also an excess of reducing bodies present, there is of course an excess of cuprous oxide formed, the red color of which hides that of the xanthine compound.

In order to isolate the suspected xanthine base, about ten liters of cane-juice were treated in the way outlined above, enough Fehling's solution being added to give a decidedly red precipitate, the solution filtered, the precipitate well washed, and dissolved iu dilute nitric acid. To this solution ammoniacal silver nitrate was added, when a dirty brown precipitate was thrown down.

This silver nitrate precipitate was found to dissolve in nitric acid (sp. gr. 1.10) somewhat slowly on boiling, and the solution so obtained deposited crystals slowly. This indicated the presence of guanine and possibly also of xanthine. A portion of the silver nitrate precipitate was treated with dilute hydrochloric acid, filtered from silver chloride, and the solution evaporated, when crystals were formed having the characteristic microscopic appearance of guanine hydrochloride. The crystals were all of one form, and none of the characteristic crystals of xanthine hydrochloride were observed, proving that no other xanthine body than guanine was present in any quantity.

The guanine hydrochloride so obtained, when treated in water solution, with an excess of ammonia yielded a flocculent white precipitate of guanine, insoluble in water, alcohol, ether, and hot dilute ammonia. This guanine was further identified by Strecker's test: evaporation to dryness with nitric acid and treatment of the residue with caustic potash, when on heating a yellowish red coloration is obtained; also by its conversion into xanthine by nitrous acid:

$$C_5H_5N_5O + HNO_2 = C_5H_4N_4O_2 + N_2 + H_2O,$$

and the formation of the characteristic crystals of xanthine hydrochloride on treatment with hydrochloric acid.

This isolation and identification of guanine has been repeated on ten samples of juice from mature cane, and on four samples of refuse molasses, and in each case there has been no indication of the presence of any other xanthine body than guanine. It is reasonable then to conclude that in mature sugar-cane guanine is the predominant and probably the only xanthine body present.

During the present season an attempt has been made to estimate the amount of guanine in cane-juice, operating in the following manner: The juice was clarified with lead subacetate, the excess of lead removed by sodium carbonate, and to the filtrate from lead carbonate, heated to boiling, enough Fehling's solution was added to give a decidedly red precipitate; the solution was filtered, and the precipitate well washed with hot water, and the nitrogen contained therein determined and calculated to guanine. One hundred grams of juice were used for each determination and the nitrogen determined by the Gunning method. An average of six samples of juice of approximately the same purity and composition gave

	Per cent.
Total nitrogen	0.0350
Guanine nitrogen	0.0012
Equivalent to guanine	0.0025

From the known properties of guanine, it was thought that this body would go through the processes of sugar manufacture unchanged, but that inasmuch as some of the other nitrogenous bodies are removed during manufacture, the ratio of guanine nitrogen to total nitrogen would be higher in the refuse molasses

than in the original juice. This conjecture was confirmed by guanine determinations in molasses. The average of four samples of refuse molasses of similar composition gave

	Per cent.
Total nitrogen	0.7140
Guanine nitrogen	0.0308
Equivalent to guanine	0.0660

In the samples of raw juice examined the ratio of total nitrogen to guanine nitrogen is 100 : 3.42, while in the refuse molasses the ratio is 100 : 4.31.

The small amount of guanine present in cane-juice is of little technical importance. The amount present in refuse molasses may however be worthy of note in considering the fertilizing or feeding value of the same.

In the analysis of sugar-cane and its products the presence of guanine may introduce an error in some cases unless its presence be recognized. Three of these cases it may be well to note :

1. In the estimation of reducing sugars in technical work the volumetric method with Fehling's solution is generally used; but sometimes when greater accuracy is wished the gravimetric method is used. Now we have already noted that xanthine bodies if present unite with the cuprous oxide formed, and while in the volumetric method this fact introduces no error—for the amount of copper precipitated is not affected—in the gravimetric method by which the cuprous oxide is reduced in a stream of hydrogen, the error introduced is proportional to the amount of guanine or other xanthine base present. The guanine is not affected by the reducing process, and is weighed as copper. It is recommended then that when a gravimetric estimation of reducing sugars is to be made in low grade sugar-house products the electrolytic estimation of the copper be resorted to.

2. A solution of sodium phosphotungstate in sulphuric acid is commonly used as a precipitant of nitrogenous bodies. Guanine in solution is partially precipitated by this reagent not as a compound of phosphotungstic acid but with the sulphuric acid, this compound being sparingly soluble. This may lead to the nitrogen of guanine being credited to other bodies; *e. g.*, peptones. A preliminary treatment with sulphuric acid and filtering before addition of sodium phosphotungstate will remove this source of error.

3. When cane-juice has been clarified with lead subacetate and mercuric nitrate added to the clear solution, a white precipitate is thrown down. This precipitate contains any amide bodies present and by some chemists this use of mercuric nitrate has been proposed or used as a proof of the presence of amide bodies. This is altogether unwarranted, for the mercuric nitrate precipitate contains any guanine present, so that the formation of a precipitate in this case is not only no indication of the amount of amide present, but no evidence of their presence at all.

KOHALA, HAWAII,
March 15, 1899.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE AGRICULTURAL EXPERIMENT STATION.]

A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.[1]

BY C. A. BROWNE, JR.

Received April 17, 1899.

THE results on the chemistry of butter-fat herewith presented constitute partly the work on regular experiments at the Pennsylvania Experiment Station, and partly extra work performed at odd moments as the other duties of the laboratory permitted.

Nearly all of the analyses were on samples of butter made at the Station Creamery, and representing for the most part the product of a herd of high-grade Guernseys. The figures given in the tables, accompanying this article, need not be taken, therefore, as typical of butter-fats in general, though we believe them to be, on the whole, fairly representative. The differences, if there are any, in the chemical composition of butter-fat from different breeds of cows, is a subject at present being investigated at this station.

We have chosen, for the sake of convenience, to divide our subject into three distinct heads; *viz.*,

1. The physical and chemical constants of butter-fat.
2. The chemical composition of butter-fat.
3. The chemistry of rancidity in butter-fat.

Each of these divisions will constitute a separate paper.

[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

I. THE PHYSICAL AND CHEMICAL CONSTANTS OF BUTTER-FAT.

A word should be said in regard to the preparation of samples of butter-fat for analysis. The method of procedure adopted in this laboratory is as follows: A sufficient quantity of the butter is placed in a glass jar or beaker and warmed at about 50° C., with occasional agitation, until the water and curd have separated out, leaving the layer of butter-fat quite clear. Then, without disturbing any of the water and curd, as much as possible of the melted fat is drawn off with a pipette into another vessel and allowed to stand, if necessary, for further clarification. The sample is then filtered through desiccated filter-paper into a clean, dry jar, after which it is stoppered and preserved for analysis in a cold place away from the light. The special precaution to be noted, in the preparation of the samples, is the avoidance of too high a temperature in melting. Butter-fat is an exceedingly unstable body and a temperature much above 50° C. will very soon produce chemical changes. Too long an exposure at 50° C. even, will alter the composition of butter-fat,[1] so that no more time than is necessary should be consumed in the processes of melting and filtering.

In Table I are given the results obtained for a few of the common constants usually determined in butter-fat analysis.

TABLE I.[2]

Constant.	Range.	Mean.	Number of samples represented.
Specific gravity $\frac{40°}{15.5°}$	0.9050–0.9102	0.9073	35
Melting-point	31.6°–34.6°	33.2°	35
Acid number	0.20–0.66	0.50	5
Saponification number	224.0–234.9	228.5	40
Ether number[3]	223.5–234.4	228	40
Iodine number	29.36–37.30	33.35	40
Reichert number (two and a half grams)	15.10–17.50	16.2	40
Reichert-Meissl number (five grams)	22.80–32.10	28.3	10
Insoluble acids, per cent	86.03–88.84	87.65	10

[1] We have found by experiment that a butter-fat kept at 50° C. for two days suffered a decrease in its iodine number of over one unit.

[2] The figures from which this and succeeding tables are made up represent the mean of duplicate determinations.

[3] Saponification number less 0.5, the mean acid number.

The constants were all determined by the usual processes employed in the analysis of oils and fats; since these are too well known to require any detailed description, we will simply indicate the methods employed, describing only any modifications which were introduced.

The specific gravity was determined on the melted samples at 40° C. by means of a Westphal balance, which gives results accurate to the fourth decimal. Whenever greater accuracy was required a pycnometer or Sprengel tube was used.

The melting-point was determined according to the method of the official chemists.[1]

The acid number, or milligrams of potassium hydroxide necessary to neutralize the free acid in one gram of fat, was determined by heating about ten grams of the fat with fifty cc. of neutral alcohol in a ten-ounce flask provided with a condensing tube. After allowing the alcohol to boil for several minutes, the flask was cooled to about 50° C., when the condensing tube was removed, and the contents titrated with tenth-normal alkali (sodium hydroxide or potassium hydroxide), using phenolphthalein as indicator.

The determinations of the acid number were made upon samples of fat taken immediately after the butter was churned, so it will be observed that, even when fresh, butter-fat contains an appreciable amount of free acid. This is a fact of some importance upon which we will dwell more fully when treating of the subject of rancidity.

The saponification number, or milligrams of potassium hydroxide necessary to saponify one gram of fat, was determined according to the usual method. About two and a half grams of fat were taken and saponified with exactly twenty-five cc. of half-normal alcoholic potassium hydroxide. To secure concordant results great care must be exercised in regard to the measuring of the potassium hydroxide solution; for this reason we prefer a burette to the twenty-five cc. pipette generally recommended. The saponifications were performed in flasks provided with condensing tubes; twenty to thirty minutes were usually allowed for the reaction, after which the contents of the flask were titrated back with half-normal hydrochloric acid, using phenolphthal-

[1] Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, p. 34.

ein as indicator. Blank experiments were run with every series of determinations.

The ether number, or milligrams of potassium hydroxide necessary to saponify the neutral fat in one gram of sample, is found by subtracting the acid number from the saponification number.

The iodine number, or percentage of iodine absorbed by the fat, was determined according to the method of the official chemists.[1] A burette was used for measuring the iodine solution as more concordant results could be secured than when a pipette was employed.

The volatile acid numbers were determined partly by the Reichert method, when two and a half grams of fat were taken, and partly by the Reichert-Meissl process, when five grams of fat were employed. With the exception of the quantity of fat weighed out the method of procedure was the same in both cases, Wollny's process[2] for saponification and distillation being the one adopted.

It is a well-known fact that the method of determining the volatile acids in butter-fat by the ordinary process of distillation is not a quantitative one. The number of cubic centimeters of half-norml alkali consumed is always greater by the Reichert process, as a larger percentage of the volatile acids are driven over when working with a smaller quantity of fat; the results in Table I show that the Reichert process gives a mean constant ten per cent. higher than the Reichert-Meissl method, after calculating the figures both to the same weight of fat.

Richard Meyer found that by distilling with a current of steam, the number of cubic centimeters of half-normal alkali was increased by twenty-five per cent. The experience in this laboratory has been that only from seventy-five to eighty per cent. of all the volatile acids pass over in one distillation. As a test, ten distillations were made on two and a half grams of fat, the contents of the flask being replaced with 110 cc. of water after each distillation. The first fraction took 15.5 cc. of tenth-normal alkali, the succeeding nine fractions requiring each in their order, 2.00, 0.95, 0.60, 0.55, 0.40, 0.35, 0.30, 0.30, 0.25, or

[1] Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, p. 32.
[2] *Ztschr. anal. Chem.* (*1889*), **28**, 721.

together 5.7 cc., giving a total of 21.2 cc., thus making the original Reichert number of 15.5 over twenty-five per cent. too small.

Instead of distilling the lower fatty acids it is possible to remove them from the higher insoluble acids by washing.[1] The process can be carried out in connection with the determination of the saponification number, or with the determination of the insoluble acids. If worked in connection with the former the method of procedure is as follows:

Having determined the saponification number of the fat the flask is replaced on the steam-bath until all alcohol is removed. The residue of soap is then dissolved in 100 cc. of hot distilled water, and after cooling to about 60° just enough half-normal hydrochloric acid is added to unite with all the combined alkali.[2] The flask is then stoppered with a condensing tube and heated on the steam-bath until the fatty acids have risen to the surface and the liquid underneath has become clear. The flask and contents are now thoroughly cooled, after which the cake of insoluble fatty acids is gently detached from the walls of the flask by shaking and the liquid filtered into a liter flask. One hundred cc. of hot water are then poured into the flask and, after the acids have melted, thoroughly shaken. The contents of the flask are poured on the filter and the flask again washed out with hot water; this is repeated until all the fatty acids are removed from the flask, when they are washed directly on the filter. As soon as the filtrate amounts to a liter it is titrated with half-normal alkali. It is needless to remark that the water used for washing should be absolutely neutral.

Although a larger percentage of the lower acids are generally removed by the above process of washing than by one distillation, the same difficulty of effecting a complete separation of the soluble from the insoluble acids is experienced. It has been found impossible to remove the last traces of soluble acids, even by continued washings, the higher and less soluble homologues, caprylic and capric acids, especially being retained by the insol-

[1] Allen: Commercial Organic Analysis (*1899*), Vol. II, Part 1, p. 191.

[2] The amount of half-normal hydrochloric acid necessary for this can be found by subtracting the number of cubic centimeters of half-normal hydrochloric acid used in titrating the excess of potassium hydroxide in the determination of the saponification number from the number of cubic centimeters of half-normal hydrochloric acid used to neutralize the potassium hydroxide in the blank experiment.

uble acids on the filter. The first filtrate (one liter) of soluble acids from a butter-fat, treated by the process of washing just described, required 15.5 cc. of tenth-normal alkali. The acids on the filter were washed nine more times, using a liter of hot distilled water at each washing. The succeeding filtrates required each in their order, 1.05 cc., 0.60, 0.50, 0.40, 0.35, 0.35, 0.30, 0.30, 0.15, making in all 19.5 cc. It is evident that, while one treatment is amply sufficient to distinguish a butter from a substitute, the method is of little value quantitatively unless the treatment of washing be repeated until the washings become neutral—a tedious operation at the best.

The process employed by us for determining the percentage of insoluble acids, or Hehner number, is as follows: Ten grams of the fat are weighed out into a wide-necked 250 cc. flask and saponified with five cc. of fifty per cent. soda and twenty-five cc. of ninety-five per cent. alcohol. The alcohol is then distilled off and the residue of soap dissolved in 150 cc. of water; 50 cc. of hydrochloric acid (1 : 1) are then slowly added with continuous shaking, after which the flask is replaced on the steam-bath and allowed to stand until the liquid beneath the layer of fatty acids has become perfectly clear. The flask and contents are now cooled; the cake of fatty acids, after hardening perfectly, is loosened from the walls of the flask by shaking gently, and the liquid underneath poured through a clean filter. The short arm of a glass siphon is then introduced, allowing the end of the tube to come in contact with the bottom of the flask; the discharging end of the siphon is closed by a piece of gum tubing fitted with a pinch-cock. The flask is now filled about three-fourths full with hot water and thoroughly agitated; after allowing the fatty acids to rise to the surface of the liquid, the siphon is filled by blowing in hot water from a wash-bottle at the lower end, the process being easily controlled by the pinch-cock. In this way also any of the fatty acids, which have risen within the siphon, can be washed back into the flask. The liquid underneath the layer of fatty acids is now siphoned off into the paper used for the first filtration, the pinch-cock serving to regulate the flow. When as much as possible of the liquid is drawn off, without taking any of the insoluble acids, the flask is again nearly filled with hot water and shaken; after washing out the siphon, the

liquid is drawn off as before. The process is continued until the washings cease to redden litmus paper; about ten washings, requiring over two liters of water, are generally necessary to effect this. When the washings are neutral the siphon is removed, any acids, which may remain adhering to it, being washed back into the flask with hot water; the flask is cooled and as soon as the acids have hardened the cake is detached and the washings poured through the filter. The flask is then placed in an inverted position over the filter and allowed to drain over night. In the morning the filter-paper, which generally contains a small quantity of insoluble acids, is washed several times with a few cubic centimeters of ether, the washings being allowed to run into the flask. The flask is then warmed at 80° until most of the ether is expelled and then dried at 100° to constant weight. We have found it expedient to dissolve out the acids, after securing a constant weight, with hot alcohol and reweigh the flask; a difference of several milligrams is generally experienced between the first and last weighings, due to the removal of soluble matter from the glass.

We believe a quicker and more thorough washing of the insoluble acids, with less danger of loss, is secured by this method than by the usual processes for determining the insoluble acids. Duplicate results can be secured which agree perfectly. The method is applicable not only to the analysis of fats and oils, but we have used it to advantage in soap analysis.

One point which we have observed in connection with the drying of fatty acids to constant weight at 100° C. is that when the acids were dried in a low evaporating dish or beaker a constant weight could never be secured; the acids continued to lose in weight even when it was evident that all moisture was removed; when, on the other hand, the drying was performed in a flask a constant weight was soon secured, after which no change was observed, even on many hours' drying. This difference we believe to be due to a partial volatilization of the insoluble acids; the escape of volatile products would be much easier from an open dish than from a flask; moreover, we have always found, after removing the flask containing the insoluble acids from the oven, that the inner surface and lower parts of the neck of the

flask were coated with a thin layer of condensed acids, showing that a volatilization must have occurred.

In Table II are given figures for a few of the constants less frequently determined in the analysis of butter-fat.

TABLE II.

Constant	Range.	Mean.	Number of samples represented.
Acetyl number	3.5–4.8	4.1	5
Glycerol calculated[1]	12.24–12.79	12.46	40
" by analysis	12.30–12.70	12.45	10
Total fat acids calculated[1]	94.72–94.94	94.85	40
Soluble fat acids calculated	6.52–8.96	7.20	10
Specific gravity $\frac{20°}{20°}$ insoluble acids	0.9106–0.9242	0.9162	10
Melting-point insoluble acids	40.2°–42.7°	41.7°	10
Saponification number insoluble acids	212.5–217.0	214.5	10
Mean molecular weight insoluble acids	258.1–263.5	261.0	10
Specific gravity $\frac{20°}{20°}$ soluble acids	0.9475–0.9483	0.9479	2
Saponification number soluble acids	563.7–577.3	571.7	15
Mean molecular weight soluble acids	97.17–99.52	98.12	15

The acetyl number, or milligrams of potassium hydroxide necessary to combine with the acetic anhydride in one gram of acetylized fatty acids, was determined according to the method of Benedikt and Ulzer.[2] The process, as conducted in this laboratory, is as follows:

Fifty cc. of the melted fat are saponified, the resulting soap is decomposed with hydrochloric acid, and the insoluble acids secured according to the usual methods. Twenty-five cc. of the dried and filtered acids are boiled with twenty-five cc. of glacial acetic acid, for two hours, in a 250 cc. flask connected with a reflux condenser. The mixture is then poured into a large two-liter flask filled three-fourths full with boiling water; the flask is thoroughly agitated for some minutes and then allowed to stand until the acids have risen to the surface. After cooling perfectly under running water, the cake of acids is gently

[1] Calculated from figures given for ether numbers in Table I.

[2] *Monatsh. Chem.*, 8, 40; Analyze der Fette, 3rd Ed., p. 146.

detached from the walls of the flask and the liquid underneath poured out; the flask is then filled half full with hot water and the contents boiled for half an hour; a few pieces of clean pumice stone, which have been kept under water, are added to prevent bumping. The liquid underneath the acids is then removed by a siphon and the acids washed by siphonation, as under determination of insoluble acids, until the wash-water is neutral. The acids in the flask, after hardening, are allowed to drain; they are then melted, transferred to a smaller vessel, and dried at 100° until all water is removed, after which the acids are filtered through dry paper and preserved for analysis.

To determine the acetyl number, three to five grams of the acetylized acids are weighed out into a 250 cc. flask, dissolved in fifty cc. of neutral alcohol, and titrated with half-normal alcoholic potash, using phenolphthalein. The milligrams of potassium hydroxide for one gram of acid are calculated as in the determination of the acid number, and the number so obtained is designated the acetyl-acid number. An excess of the alcoholic potassium hydroxide is then added, the flask is stoppered with a condensing tube, and heated on the bath twenty to thirty minutes, after which the excess of potassium hydroxide is titrated back with half-normal hydrochloric acid. The quantity of potassium hydroxide consumed by this second process, when expressed in milligrams per gram of fat, constitutes the acetyl number. The sum of the acetyl-acid number and acetyl number is known as the acetyl-saponification number. The acetyl number then represents simply the ether number of the acetylized acid, being the difference between the acetyl-acid and acetyl-saponification numbers.

In reviewing the literature of the subject only two other values could be found for the acetyl number of butter-fat. Wachtel gives 9.6, and Bondzynski and Rufi 18.2, numbers both considerably higher than the values given in Table II. The acetyl figure, though of little value in practical butter analysis, yet furnishes us a measure of the oxy-acids in a fat; more will be said as to the employment of this constant under the subject of rancidity.

The percentage of glycerol which a butter-fat will yield upon saponification can be readily calculated from the ether number.

In the saponification of any triglycerid three molecules of potassium hydroxide separate one molecule of glycerol, or 168.3 parts of potassium hydroxide corresponds to ninety-two parts of glycerol; one gram, therefore, of potassium hydroxide would equal 0.5466 gram of glycerol.[1] If E represents the ether number of a fat, the percentage of glycerol, G, which the fat will yield, will be,

$$G = 0.05466\ E.^{2}$$

This indirect method of estimating glycerol can be used in the analysis of any fat or oil which belongs to the class of triglycerids: with diglycerids the method is not practicable as Benedikt has shown.[3] With rancid fats, owing to the presence of aldehyde bodies, as will be shown later, the method gives too high results.

The percentage of glycerol was determined directly by the method of Benedikt and Zsigmondy,[4] which is based upon the fact that one molecule of glycerol, when oxidized in a strongly alkaline solution with permanganate, produces quantitatively exactly one molecule each of oxalic acid and carbon dioxide.

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$

Allen's[5] modification of the original process of Benedikt and Zsigmondy, was followed in this laboratory with the exception of a few minor differences.

Ten grams of butter-fat are weighed out into a six-ounce saponification flask of heavy glass provided with a tightly fitting glass-stopper. Five grams of potassium hydroxide dissolved in fifty cc. of water are then added and the glass stopper wired in securely. The flask is placed in the steam-bath and shaken thoroughly every fifteen minutes, the heating being continued until the contents of the flask become thick and homogeneous, and no more liquid fat is seen swimming on the surface: eight to twelve hours is generally necessary for this. When saponification is complete the flask is cooled, unstoppered, and the contents washed out into a large beaker with 200–300 cc. of hot water. A perfectly clean solution should be obtained without any oily particles being visible.

[1] Zulkowski: *Ber. d. chem. Ges.*, 16, 1140.
[2] Benedikt: Analyse der Fette und Wachsarten, 3rd Ed., p. 182.
[3] *Ibid.*, p. 182.
[4] *Chem. Ztg.*, 9, 975. Analyse der Fette, p. 182.
[5] Allen: Commercial Organic Analysis, 3rd Ed., (*1899*), Vol. II, Pt. 1, p. 314.

The solution of soap is decomposed with an excess of dilute sulphuric acid, and the fatty acids separated and washed in the usual way; the washings, which should be clear, are made up to one liter and thoroughly mixed. 200 cc. (two grams of fat) of this solution are measured out into a large evaporating dish or beaker, diluted to about 400 cc. and neutralized with potassium hydroxide solution using phenolphthalein. Ten grams of solid potassium hydroxide are then added, and when completely dissolved, a saturated solution of permanganate is added, at ordinary temperature, until the liquid is colored no longer green, but a very dark-blue (three to five grams of permanganate are sufficient for this). The solution is then heated to gentle boiling for about an hour, the liquid becoming finally red with precipitation of the hydrated peroxide of manganese; the volume of the liquid, during the boiling, should be kept at about 400 cc. by adding water from time to time. A strong solution of sodium sulphite is then gradually added until all color is destroyed, and the liquid above the brown precipitate is clear. The solution is next filtered through a large funnel, using heavy filter-paper, into a liter flask, and the precipitate washed with hot water until the flask is nearly full; the slight turbidity, which frequently shows in the final washings, does no harm. After cooling and making up to one liter, 500 cc. (one gram original fat) are measured into a large beaker, acidified with acetic acid, heated nearly to boiling, and precipitated with ten cc. of a ten per cent. calcium chloride solution; the liquid is heated on the steam-bath an hour or more until everything has settled out. The precipitate, consisting of calcium oxalate, with a little sulphate mixed, is filtered into a prepared Gooch crucible and thoroughly washed with hot water. The contents of the Gooch crucible, including the asbestos felt, are then washed back into the original beaker with about 200 cc. of hot water, acidified with dilute sulphuric acid, and heated on the bath for ten minutes, after which the solution is titrated with tenth-normal permanganate. One cc. of tenth-normal permanganate equals 0.0046 gram of glycerol.

The oxidation method for determining glycerol is a somewhat long and tedious one, requiring also a certain amount of practice to secure good results. The details of the method, as regards

the oxidation, must be rigidly adhered to. Benedikt[1] states that the soluble fatty acids, butyric, etc., which are present in the same solution with the glycerol, do not yield oxalic acid on the treatment with potassium hydroxide and potassium permanganate, but that this is true only so far as regards the original method. Johnstone[2] and Mangold have both found that in strongly alkaline solutions butyric acid can be oxidized to oxalic acid. Experiments in this laboratory confirm this; if too great an excess of either potassium hydroxide or potassium permanganate is used for oxidation, or if during the process of boiling, the liquid is allowed to become too concentrated, abnormal results are secured. A butter-fat which gave 12.35 per cent. of glycerol, when analyzed according to the method, yielded, according to analysis, over eighteen per cent. of glycerol, by employing a large excess of potassium hydroxide and potassium permanganate, and oxidizing in a concentrated solution, thus proving beyond doubt that the soluble acids had been acted upon. By observing the necessary precautions, however, no danger need be apprehended from this source; we have found the method to yield most excellent results on many of the ordinary fats, as well as on butter-fat itself, the agreement between the percentage of glycerol as calculated from the ether number, and as determined by analysis, being very close, as the following examples will show.

Fat.	Ether number.	Glycerol calculated. Per cent.	Glycerol by analysis. Per cent.
Beef-tallow	195.5	10.68	10.61
Commercial stearin	192.3	10.51	10.56
Butter-fat	232.2	12.69	12.70

The total percentage of fatty acids which a butter-fat will yield can be readily calculated if we know the percentage of glycerol produced on saponification.[3] By inspecting the formula,

$$C_3H_5(RO_2)_3 + 3H_2O = C_3H_8O_3 + 3RO_2H$$

$$\text{Fat} + \text{water } (54) = \text{glycerol } (92) + \text{fatty acid},$$

we observe that in saponifying a fat fifty-four parts of water are required for every ninety-two parts of glycerol produced. The yield of fat acids (F) from 100 parts of fat would be represented

[1] Analyse der Fette, 3rd Ed., p. 184.
[2] *Chem. News*, 63, 11.
[3] Zulkowski: *Ber. d. chem. Ges.*, 16, 1315.

then by the formula, $F = 100 + \frac{54}{92} G - G$, or $F = 100 - \frac{38}{92} G$, in which G equals percentage of glycerol. G, as we have shown, can be obtained from the ether number (E) of a fat by the formula, $G = 0.05466\ E$; by substituting this value for G in the previous equation we obtain, $F = 100 - \frac{38}{92} \times 0.05466\ E$ or $F = 100 - 0.02258\ E$.[1]

The percentage of soluble acids in a butter-fat can be found by subtracting the percentage of insoluble acids (Hehner's number) from the percentage of total acids.[2]

The specific gravity of the insoluble acids was determined by weighing the acids in air and in water at 20°, using a sinker. For a sinker we have found a small platinum crucible cover to answer very satisfactorily, since it offers a convenient receptacle for holding the acids; a silk thread is used for suspending the cover from the beam of the balance; no air-bubbles should be present on the surface of the sinker during the operation and to prevent their appearance recently boiled distilled water is used throughout the work. The following example will illustrate the method:

Weight of sinker and fatty acids in air	= 6.5460 grams	
" " " alone " "	= 5.2110 "	
" " insoluble fatty acids " "	= 1.3350 "	$= w$
" " sinker in water at 20°	= 4.9715 "	$= \omega$
" " " and acids in water at 20°	= 4.8405 "	$= \omega'$

From the formula $s = \frac{w}{w + \omega - \omega'}$, we calculate the specific gravity of the insoluble acids to be 0.9106. This formula is sufficiently accurate for ordinary purposes; more strictly it should read, $s = \frac{w(1 - s)}{w + \omega - \omega'} + s$, in which s equals the density of air; the value of s for dry air, within the ordinary range of temperature and pressure, is 0.0012. If we desire to express the gravity in terms of water at 4° we should use the formula $s = \frac{w(d - s)}{w + \omega - \omega'} + s$, where d equals the density of water at the temperature of the

[1] Benedikt: Analyse der Fette, 3rd Ed., p. 162.
[2] *Ibid.*, p. 165.

experiment, a value easily found from tables. At 20° d is 0.9982, our original specific gravity, then, corrected to $\frac{20°}{4°}$ would be 0.9091 instead of 0.9106.[1]

The melting-point of the insoluble acids was determined by observing the temperature at which the acids became transparent when heated in a capillary tube. A small piece of capillary tubing, about one inch in length, is sealed at one end and nearly filled with the melted fatty acids; there should be no air space beneath the fatty acids and to prevent this, the filling of the tube is best accomplished with a small pipette or dropper, the end of which has been drawn out to a slender point. The tubes should be filled and cooled several hours before making the determinations.

In conducting the experiment the small tube containing the fatty acids is fastened to the bulb of a delicate thermometer and then lowered into a large test-tube, nearly full of distilled water recently boiled and cooled; the test-tube is fastened into a tall beaker nearly filled with water. Heat is now gently applied, keeping the water in the outer vessel constantly stirred by means of a blowing bulb. As soon as the temperature of the water in the beaker reaches 38°, the heat is raised more slowly, about 1° in five minutes. A difference of about 1° is generally observed between the beginning of melting and the point of absolute transparency; we have used the latter as the true melting-point, though the mean of the two readings would be perhaps a little more correct. The method of the official chemists would not be practicable in the case of determining the melting-point of the insoluble acids, owing to the solubility of the acids in alcohol.

The saponification number of the insoluble acids, which in this case would be identical with the acid number, was determined by dissolving three to five grams in hot neutral alcohol and titrating with half-normal potassium hydroxide.

From the saponification number (s),[2] the mean molecular

[1] This method can be used as well for determining the specific gravity of butter-fat at the ordinary temperature. We have found the mean specific gravity of butter-fat corrected to $\frac{20°}{4°}$ to be 0.9250.

[2] Analyse der Fette, p. 163.

weight (m) of the insoluble acids can be readily calculated by means of the formula $m = \frac{56100}{s}$.[1]

For the determination of the constants of the soluble acids from butter-fat, it is necessary first to separate the acids in a state of complete purity. To effect this the following process was employed:

One hundred grams of butter-fat were saponified with fifty cc. of fifty per cent. sodium hydroxide solution and 200 cc. of alcohol in a large flask provided with a condensing tube. After distilling off the alcohol, the residue was dissolved in hot water, decomposed with excess of hydrochloric acid (1 : 1), and heated on the bath using the condensing tube, with occasional shaking until the liquid underneath the layer of acids had become clear. The contents of the flask were then cooled, the cake of acid detached, and the liquid underneath filtered through heavy paper into a large evaporating dish. The insoluble acids were then remelted, brought upon the filter with hot water and washed until the filtrate became neutral. The combined filtrates and washings were neutralized with sodium hydroxide solution using phenolphthalein and evaporated to about 500 cc.; the solution was next filtered into a large separating funnel, acidified with dilute sulphuric acid, and after cooling shaken with fifty cc. of washed ether. After standing for a few minutes, the two solutions were separated and the aqueous liquid again treated with fifty cc. of ether; the process was repeated for a third time when the combined ethereal solutions were filtered into a dry dish and the ether allowed to evaporate at the room temperature; the residue of soluble acids[2] (five to six grams) was dried in a vacuum over sulphuric acid and then preserved in a stoppered vial. The soluble acids thus obtained consisted of a light mobile liquid having a pale

[1] In the *Chem. Rev. Fett u. Harz-Ind.*, 5, [9], 169–172, R. Henriques calls attention to a difficulty in estimating the mean molecular weight of the insoluble acids from butter-fat, in that the values found on drying the acids at 105°–110°C. (*viz.*, 267–270) differed from those (256.3–263) obtained when the drying was effected at the ordinary temperature in a vacuum. (Abstract in *Analyst*, No. 274, p. 7.)

The values found by Henriques on drying in a vacuum are identical with those given by us in Table II. The higher values, found on drying the acids at 105°–110°, we believe to be due to a partial volatilization of acids of low molecular weight, such as lauric and myristic, which, as will be shown in a later article, are present in the insoluble acids of butter-fat in considerable quantity. Such a volatilization may occur at even 100°, as we have already indicated (p. 618).

[2] A quantitative separation of the soluble acids is not effected by the treatment.

straw color,[1] and giving the intense odor characteristic of butyric acid.

The specific gravity of the soluble acids was determined at 20° C. by means of a small two cc. pycnometer.

The saponification number was determined by titrating one to two grams of the acids, dissolved in neutral alcohol, with half-normal potassium hydroxide. Knowing the saponification number (s) the mean molecular weight of the soluble acids is determined by the formula $m = \frac{56100}{s}$.

We are well aware that the figures given in Table II for the mean molecular weight of the soluble fatty acids are much lower than those given by certain German authorities. Benedikt[2] gives 139 as the mean molecular weight of the volatile fatty acids from butter-fat. This number was not found directly, however, but was calculated on the assumption that the Reichert-Meissl number is a quantitative expression for the amount of volatile acids, an assumption not warranted by experiment as has been shown.[3]

If the calculation be made on the volatile acid number from ten distillations instead of from one, results will be obtained which approximate very closely those expressed in Table II, as the following example will show. A butter-fat, containing 8.72 per cent. of soluble acids, required to neutralize the volatile acids (ten distillations) from 2.5 grams, 22.3 cc. of tenth-normal sodium hydroxide, or 8.92 cc. of tenth-normal sodium hydroxide per gram of fat. $\frac{8.72}{8.92} \times 100 = 97.7$, the mean molecular weight of the soluble acids. Practically the same figure is arrived at, if we obtain the saturation number of the soluble acids, after their complete removal by washing, according to the method already described.[4] Two and five-tenths grams of a butter-fat, containing seven and seven-tenths per cent. of soluble acids, required 19.5 cc. of tenth-normal sodium hydroxide to neutralize the soluble acids removed by washing. The cubic

[1] If distilled in a vacuum the acids can be obtained colorless.

[2] Analyse der Fette, 3rd ed., p. 546.

[3] This article, p. 615. Benedikt, elsewhere in his own work, calls attention to this same fact. Analyse der Fette, 3rd ed., p. 137.

[4] This article, p. 617.

centimeters per gram of fat would be seven and eight-tenths and the mean molecular weight would equal $\frac{7.7}{7.8} \times 100$ or 98.7.

We have determined the mean molecular weight of the volatile acids in many butter-fats by still another process. The weight of the barium salts of the volatile acids, is determined and, from the amount of barium oxide contained therein, the mean molecular weight of the combined acids is calculated by means of the formula $m = \frac{76.7(r-b)}{b} + 9$, in which m is the mean molecular weight sought, r the weight of barium salts, and b the weight of barium oxide. The process can be carried out in connection with the determination of the Reichert or Reichert-Meissl number. After neutralizing the distillate of volatile acids with half-normal barium hydroxide, the solution is evaporated to dryness in a weighed platinum dish, and heated at 100° C. to constant weight. The residue is then moistened with a little strong sulphuric acid, ignited, and weighed; from the weight of barium sulphate is calculated the barium oxide. A comparison of the values obtained for the mean molecular weight of the volatile or soluble acids by the above method and by the method of direct titration is given herewith:

	Range.	Mean.
By direct titration	97.94–99.51	98.73
" weighing the barium salts	97.17–98.97	97.92

We can verify this figure for the mean molecular weight of the volatile or soluble fatty acids in the following manner:

For the average butter-fat we may consider the following constants to be nearly correct:

Saponification number	228.5	(Table I)
Insoluble acids, per cent	87.65	"
Soluble " "	7.20	(Table II)
Saponification number of insoluble acids	214.5	"

There are required then for the average butter-fat:

	228.5 mg. KOH	to saponify 1 gram of fat
$0.8765 \times 214.5 =$	188.0 " " " "	insoluble acids in 1 gram fat
Difference	40.5 " " " "	soluble acids in 1 gram fat

or 40.5 mgs. of KOH are required to saponify 0.0720 gram of

soluble acids. Therefore $\frac{40.5}{0.072} = 562.5$, theoretical saponification number of soluble acids, and $\frac{56100}{562.5} = 99.73$, theoretical molecular weight of the soluble acids in the average butter-fat. While this theoretical figure is a trifle higher than any we have found in actual work, the agreement is sufficiently close to enable us to say that the mean molecular weight of the soluble acids from butter-fat lies very near to the value expressed in Table II.

We have often found it convenient in our work, where an accurate determination was impossible, either from want of time, or lack of material, to make a rough approximation of the percentage of soluble acids; for this purpose we have devised a very simple formula, the only factor necessary to know being the saponification number of the butter-fat. The equation, in which v equals per cent. of soluble acids and s the saponification number, is :

$$v = 0.0018\left[s - \left(188.5 + \frac{228 - s}{2}\right)\right] \times 100, \text{ or } v = 0.09(3s - 605).$$

The formula is deduced from data given in the preceding tables. The average butter-fat, having a saponification number of 228, and containing 87.65 per cent. of insoluble acids with a saponification number of 215, would require 188.5 milligrams of potassium hydroxide to neutralize the insoluble acids from one gram of fat. For any butter-fat, having a saponification number s, this value was found to be about $188.5 + \frac{228 - s}{2}$. From the molecular weight of the volatile or soluble acids, we find that one milligram of potassium hydroxide neutralizes 0.0018 gram of soluble acids ; the difference, therefore, between the saponification number of the butter-fat and the milligrams of potassium hydroxide required for the insoluble acids, multiplied by 0.0018, gives the weight of soluble acids per gram of fat; multiplying this by 100 we arrive at the percentage of soluble acids sought.

The formula is not expected to give results absolutely accurate in any case, since variations in the saponification number of a butter-fat are caused to a considerable extent by differences in the molecular weight of the insoluble acids, differences which the formula, as given, does not take into account.

THE RELATION BETWEEN THE CONSTANTS OF DIFFERENT BUTTER-FATS.

It was observed, in tabulating the results from many analyses of butter-fat, that there existed a certain ratio between some of the different constants. An inspection of the following table will illustrate this point.

TABLE III.

Butter-fat.	Saponification number.	Reichert number.	Iodine number.	Melting-point.	Specific gravity. $\frac{40^\circ}{15.5^\circ}$ C.
1	226.1	15.3	34.85	33.5°	0.9092
2	226.3	15.6	34.58	34.5°	0.9058
3	226.9	15.7	35.45	33.8°	0.9070
4	230.9	16.1	33.67	32.5°	0.9058
5	232.7	16.2	30.96	33.0°	0.9085
6	232.9	16.3	29.56	32.4°	0.9068

We notice that with an increase of the saponification number a quite uniform increase of the Reichert number takes place, while the iodine absorption decreases; these are such variations as one would expect ; a higher percentage of oleic acid of low combining power would raise the iodine number and tend to diminish the saponification value; similarly an increase in the percentage of the soluble acids of high combining power would elevate both the Reichert and the saponification numbers.

Table IV comprises a few of a large number of butter-fats analyzed at this station by Mr. W. S. Sweetser in 1894, and illustrates this relation even more pointedly than Table III.

TABLE IV.

Butter-fat.	Saponification number.	Iodine number.	Reichert number.
1	218.8	41.32	17.1
2	222.4	37.30	17.5
3	224.6	37.00	18.6
4	232.5	30.21	19.4
5	236.2	27.17	20.8
6	241.5	25.91	21.3

From these tables it would seem as if the percentages of oleic and of the soluble acids in different butter-fats bore a ratio somewhat complementary to one another. It must be remembered that the relations, which the foregoing tables represent, are only general, and by no means fixed ; there are butter-fats which show constants bearing relations different from those expressed

above, and from isolated cases a table might be constructed showing exactly opposite tendencies. As regards specific gravity and melting-point, no definite relation could be discovered, though the latter showed a tendency to diminish as the saponification and Reichert numbers increased.

ABNORMAL BUTTER-FATS.

Different observers have reported from time to time cases in which butter-fats showed chemical and physical constants of such abnormality that, were the samples not known to be genuine, an analysis would condemn them at once as spurious.

F. W. Morse[1] has reported two butter-fats, from individual cows, giving Reichert-Meissl numbers of 16.5 and 11.2. "The samples were very hard, pale in color, and had an odor resembling that of tallow;" these abnormalities and the phenomenally low figures for volatile acids were attributed to an advanced period of lactation, and the presence of cottonseed products in the feed.

Samples 1 and 6 of Table IV are what might be classified as abnormal, though no note was made at the time of analysis as to any peculiarities in physical appearance. The saponification number of Sample 1 is far below the limit usually assigned to this constant, while the iodine absorption is excessively high; the irregularities of these two figures are explained by the prevalence of gluten feed in the ration.

The saponification and iodine numbers of Sample 6 vary at the opposite extreme; root crops, such as sugar-beets and mangels, predominated in the rations fed to the animals producing this butter, and no doubt account for the unusual figures.

While the butter-fat from the milk of single cows may frequently show abnormalities, such instances are less common with a full herd, since individual differences would be concealed in a general average; nevertheless, such instances do occur. Farnsteiner[2] and Karsch report the following constants of two butter-fats:

[1] New Hampshire Experiment Station Report (*1893*), p. 152.

[2] *Ztschr. Untersuch. der Nahrungs u. Genussmittel* (*1898*), 16-21; Abstract in *Analyst*, No. 263, p. 38.

	Saponification number.	Iodine number.	Reichert-Meissl number.
I. From 180 cows.....	218.53	49.57	22.80
II. " 25 "	219.74	40.00	22.11

The abnormal chemical constants of these samples were attributed to a very advanced period of lactation; no mention was made as to any anomalies of taste, odor, etc.

Sickness, peculiarities of feed, and advancement in the period of lactation are the principal causes of irregularities in the composition of butter-fat. The subject is one of special interest and illustrates the difficulty, occasionally experienced, of absolutely identifying the character of a questionable butter-fat. It will be of interest in this connection to compare the generally accepted limits for the three constants, used most universally in butter-fat analysis, with the extreme limits, where the names of the observers are bracketed.

	General limits.	Extreme limits.
Reichert-Meissl number.....	20–33	11.2[Morse]–41[Nilson]
Saponification number	220–236	216[Samelson]–245[Fischer]
Iodine number.....	26–38	19.5[Moore]–49.57 [Farnsteiner] [and Karsch]

INFLUENCE OF RATION UPON THE CHEMICAL COMPOSITION OF BUTTER-FAT.[1]

Allusion has already been made to the influence of certain feeds upon the chemical constants of butter-fat. Considerable work has been performed at the Pennsylvania Experiment Station along this line, in connection with various dairy-feeding experiments, according to plans of Dr. William Frear; the results of this work have, for the most part, not yet been published. A full discussion and tabulation of these experiments would be foreign to the nature and purposes of the present article, but certain general conclusions from the work may be briefly stated in this connection. The work of others has, in the main, been corroborated; this is true especially as regards the effect of different rations upon the volatile acid figure and iodine absorption. It is to be regretted that so few experimenters, in their work along this line, have reported determinations of the saponification number,—a constant, the value of which in butter-fat

[1] Bulletins 13 and 16, New Hampshire Experiment Station, contain some excellent experiments along this line. For a very full discussion of the subject see article by William Frear in *Agricultural Science*, 7, No. 3, p. 120.

analysis, as it seems of late, has been too greatly underestimated.

Briefly, the experiments conducted here indicate that, while the tendency of certain feeds, of which gluten meal is a type, is to greatly diminish the saponification number and increase the iodine absorption, other rations, such as those consisting of root products, beets, mangels, etc., have precisely an opposite effect; the extreme figures of Table IV, in butter-fats Nos. 1 and 6 were mostly, if not entirely, produced by just such a difference in ration.

It was found that other feeds, such as cottonseed, linseed, and corn-meal, all produced decided effects upon the chemical qualities of butter-fat; the three feeds named, when fed in moderate quantities, showed a tendency to elevate the saponification number, but there was a difference in other respects; while cotton and linseed meal diminished the Reichert number, corn-meal seemed to increase this constant; cottonseed and corn-meal both caused a marked decrease in the iodine absorption, whereas linseed meal produced an elevation in the iodine figure. Great care must be exercised in the interpretation of results from such experiments; other factors, such as the individuality of the cow and the stage of lactation, must not be lost sight of. The precise influence of a particular food upon the composition of the butter-fat cannot, in every instance, be foretold; we may say that the effect will always be more or less a variable quantity, since a great deal depends upon the nature of preceding rations.[1]

There is room for much study along this particular line, and further researches are greatly to be desired, not only as regards the effect of different kinds of food upon the chemical qualities of butter-fat, but also as regards that principle of the ration which is most active in producing a given change, as to whether it be of a carbohydrate, an albuminoid, or a fatty nature. The solution of the difficult physiological problem, dealing with the origin and formation of the fat secreted by the lacteal glands, will certainly be promoted by such investigations.

[1] Linseed meal, for example, if fed after a cotton meal ration, would elevate the iodine absorption, whereas, if fed after gluten meal, the iodine number would be diminished.

NOTE.

How to Ignite a Hydrogen Jet with No Possibility of Exploding the Generator.—The following are perhaps fair samples of the directions usually found in text-books and manuals for igniting a jet of recently generated hydrogen gas:

"After the action has continued for a minute or two apply a lighted match."[1]

"When all the air is expelled, not less than ten minutes, light the jet of hydrogen."[2]

"When the gas is coming off freely, light the jet."[3]

As is well known, with any of the above directions, inexperienced students do continue to explode hydrogen generators with annoying frequency, and it is believed that a method of igniting a jet of hydrogen gas with no possible danger of exploding the generator will be welcomed generally by teachers of introductory and qualitative chemistry.

The following method, used by the writer with his classes for a number of years, is absolutely safe and causes no loss of time whatever:

As soon as the action begins collect the escaping gas in a test-tube, and when it is thought to be full of pure gas, remove two or three feet from the generator and ignite the hydrogen in the test-tube; then immediately *attempt* to light the jet of hydrogen *with the hydrogen flame contained in the test-tube.* If the gas is explosive it will explode in the test-tube and *leave no flame.* If on the other hand a flame remains in the test-tube with which the jet can be ignited, it is certain that the gas in the generator is no longer explosive. Hence, the caution: Never light the hydrogen jet except with the hydrogen flame obtained as just described. The student may try to ignite the jet by this method as often as he wishes until he succeeds, and if the hydrogen is properly generated the jet will be ignited in less than a minute.

UNIVERSITY OF ILLINOIS, AGRICULTURAL EXPERIMENT STATION. C. G. HOPKINS.

A New Test for Cocaine.—There are two well-known tests for determining the freedom of commercial cocaine salts from other

[1] Remsen: Introduction to Chemistry, p. 64.
[2] Newbury: Laboratory Note-Book, eighteenth practice.
[3] Shepard: Elements of Inorganic Chemistry, p. 38.

coca alkaloids. These are the permanganate test for detecting cinnamyl-cocaine, and the ammonia test, popularly known as McLagan's test, for detecting the presence of the coca alkaloids which are resistant to permanganate. While it is generally admitted that the permanganate test is sufficient to detect the presence of cinnamyl compounds, chemists have expressed some doubt regarding the value of McLagan's test. The writer has for some time been conducting experiments with the object of finding a substitute for McLagan's test which would allow of the rapid and accurate determination of the presence in cocaine salts of the coca alkaloids not indicated by the permanganate test.

As the result of numerous determinations, I have devised a test based on the fact that the chromates of these alkaloids are much less soluble than cocaine chromate, both in water and in water acidulated with hydrochloric acid. The relative solubility of the chromates in acidulated water is about 1 to 500 in the case of cocaine chromate, and 1 to 5000 in the case of the residual alkaloidal chromates.

I therefore offer the following as a simple and satisfactory method of determining the purity of cocaine salts: 0.05 gram cocaine hydrochloride is dissolved in twenty cc. of distilled water, mixed with five cc. of a three per cent. solution of chromic acid, and to the mixture five cc. of a ten per cent. solution of hydrochloric acid are added. It is advisable to keep the temperature of the solution at 15° C. If the cocaine hydrochloride be pure a clear solution will result. If other than traces of foreign coca bases be present the solution becomes cloudy at once, or in a few minutes, according to the amount of impurity present.

It is advisable to make the test side by side with a specimen of known purity for comparison.

GEORGE L. SCHAEFER.

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